doi: 10.1111/cote.12255

The use of nutshell firstly as a natural dye for cotton and wool and then as a natural adsorbent for colour removal of basic dye effluent

Elçin Güneş[a] and Rıza Atav[b,]*

[a]Department of Environmental Engineering, University of Namık Kemal, Çorlu-Tekirdağ, Turkey

[b]Department of Textile Engineering, University of Namık Kemal, Çorlu-Tekirdağ, Turkey
Email: ratav@nku.edu.tr

Received: 25 August 2015; Accepted: 11 September 2016

The aim of this study is to utilise nutshell, which is normally a waste. To this end, in the first part of our study we investigated the usability of nutshell extract solution as a natural dye for the coloration of cotton and wool fabrics. In order to optimise the fastness properties of dyed samples, mordant type was chosen as a variable in experiments and dyeings were carried out at 100 g l^{-1} extract concentration. After extracting its dye, nutshell was used as adsorbent for colour removal of basic dye effluent. The effect of adsorbent dose, initial dye concentration, and contact time on the adsorption of malachite green (MG) onto nutshell was investigated. Adsorption isotherms and kinetics of MG adsorption onto nutshell were also studied.

Introduction

Dyeing and finishing processes are recognised as major sources of coloured effluent. Discharge of dyeing wastewater into streams possesses a severe problem. Nowadays, especially in areas that have intensive industrial wastewater discharges, receiving water flows have become colourful and pollution has reached disturbing levels. The presence of colours and dyes in water gives rise to chemical oxygen demand (COD), biochemical oxygen demand (BOD), and high-suspended solids (SS) [1]. Dye removal from coloured effluent is difficult because of its complex structure. The conventional methods used for the removal of dyes from effluent include physical, chemical, and biological methods. Adsorption, a physical method, is considered to be an effective method for the removal of dyes owing to its low maintenance, simple operation, and effectiveness. The adsorption process provides an attractive alternative, especially if the adsorbent is inexpensive and readily available [2,3]. Activated carbon is the most commonly used adsorbent for colour removal from waters [4]. However, activated carbons are expensive owing to their relatively high operating costs and regeneration and reactivation procedures [4,5]. For economic reasons, a number of non-conventional sorbents have been tried for the treatment of many pollutants, and the use of alternative adsorbents instead of the costly activated carbon is greatly encouraged [6]. There are many studies that have used a number of non-conventional sorbents in the treatment of wastewaters. Natural materials, biosorbents, and waste materials from industry and agriculture represent potentially more economical alternatives [4].

In our previous study, we examined the possibility of using walnut rind firstly as a natural dye for wool and then as a natural adsorbent for colour removal of basic dye effluent [7]. The aim of the present study is to utilise nutshell, which is normally a waste. To this end, in the first part of our study we investigated the usability of nutshell extract solution as a natural dye for the coloration of cotton and wool fabrics. After extracting its dye, in the second part of this study the aim was to determine whether nutshell could be a good alternative to costly adsorbents such as activated carbon for colour removal of basic dye effluent.

Materials and Methods

Experiments related to the use of nutshell as a natural dye

Material

In this study, 100% scoured and bleached cotton knitted fabric and 100% washed wool woven fabric were used. The physical properties of fabrics used in experiments are given in Table 1. All experiments were carried out using distilled water.

Natural dye

Nutshell (*Corylus avellana*) was used as a natural dye. The reason for choosing nutshell among hundreds of plants is its ease of accessibility, which could be important for its application in the textile industry. Furthermore, it means that a waste is being utilised. In the literature, nutshell is identified as a natural dye plant that contains juglone and gives a brown colour. The chemical structure of juglone (CI Natural Brown 7), which is 5-hydroxy-naphthoquinone, is given in Figure 1 [8,9].

Preparation of dye extract

Plant samples (100 g) were placed in 1 l of water. The solution was then heated to boiling temperature, boiled for 30 min, and then filtered with gauze fabric. This filtrated solution was used as dyeing liquor.

Dyeing with nutshell extract

Filtrated dye extract (150 ml) was used to provide a liquor to goods ratio of 30:1 for 5 g of material. Dyeings were carried out at the pH of the extract solution, which was 5.7. In dyeings to which mordant was added, the amount of mordant was 10%. The mordants used in the study were

Table 1 Physical properties of the fabrics used in the experiments

	100% Cotton	100% Wool
Yarn count	Ne 30/1	Nm 48/1
Structure	Single jersey	Plain
Weight (g m^{-2}) (TS251)	138.6	157.2

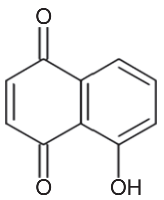


Figure 1 Chemical formula of CI Natural Brown 7

$KAl(SO_4)_2$ and $FeSO_4$. Dyeing experiments were performed on a Termal HT dyeing machine (Turkey) according to the dyeing graph given in Figure 2.

Colour measurements
CIE $L^*a^*b^*$ colour values and reflectance (R%) values of dyed samples were measured on a Gretag Macbeth (USA) E700 instrument (D_{65}/10°), and colour yields (K/S) of dyed samples were calculated by the Kubelka–Munk equation:

$$K/S = \frac{(1-R)^2}{2R} \quad (1)$$

where R is the reflectance value at the maximum absorption wavelength (nm), K is the absorption coefficient, and S is the scattering coefficient.

Fastness tests
The washing fastness was determined at 40 °C according to ISO 105-C06:A1S [10]. Dry and wet rubbing fastness of samples were assessed according to the ISO 105-X12 standard [11].

Experiments related to the use of nutshell as a natural adsorbent
Adsorbent preparation
In the study, the nutshells were cut into small pieces. These small pieces were then washed several times with distilled water and burned at 450 °C for 90 min in a muffle. The nutshells were then ground. The powder of particles was used as an adsorbent for the removal of MG in solution. In Table 2, nutshells before dye extraction, after dye extraction, and after burning and grinding are shown.

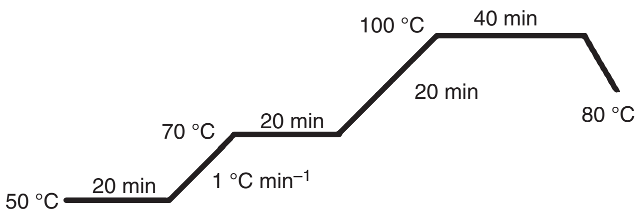


Figure 2 Dyeing graph used in the experiments

Preparation of aqueous dye solutions
Malachite green oxalate (Setacryl Green ML) (CI Basic Green 4), which was kindly supplied by SETAŞ Inc. (Turkey), was used in this study. Its chemical formula and molecular weight (g mol^{-1}) are $C_{23}H_{25}ClN_2$ and 364.91 respectively. It was assumed that the dye content was 100%, which is unlikely to be the case because of diluents while preparing dye solutions in different concentrations. The aqueous solution of MG was prepared by dissolving the desired amount of the dye in distilled water. A stock solution of 100 mg l^{-1} was prepared at pH 7. Solutions of the required concentrations were prepared by successive dilution of this stock solution.

Adsorption studies
The effect of contact time (0, 1, 5, 15, 30, 60, and 120 min) and adsorbent doses (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.2, and 2.4 g l^{-1}) on colour removal were studied by a series of kinetic and equilibrium experiments. During the experiments it was observed that the colour of MG dye solutions change sharply, depending on pH. For this reason, all adsorption studies were carried out at ambient pH (7 ± 0.4). The samples were taken at the end of the desired contact time to determine the effect of agitation time. A control flask with only the adsorbent (0.8 g l^{-1}) in 200 ml of deionised water was used as reference. During the experiments, after preparing each flask, they were agitated at room temperature (25 °C) at 200 rpm for 2 h. The contents of each flask were then centrifuged at 4000 rpm for 5 min, and absorbance of MG in the supernatant was measured.

The absorbance values of dye solutions were measured at a wavelength corresponding to the maximum absorbance (λ_{max} = 617 nm for MG) using a Thermo Spectronic Aqua-Mate UV-vis spectrophotometer (Thermo Scientific, USA).

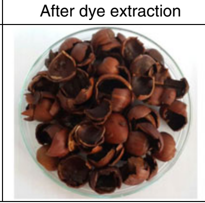
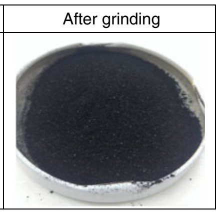
The amount of MG adsorbed was calculated from the following equation:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (2)$$

where q_e is the amount adsorbed (mg g^{-1}), C_0 and C_e are the initial and equilibrium MG concentrations in the solution (mg l^{-1}) respectively, V is the solution volume (l), and W is the mass of nutshell (g).

Experiments were conducted to assess the kinetics of MG adsorption on nutshell. Adsorption equilibrium studies were also employed to determine the adsorption capacity of

Table 2 Nutshell used in the experiments [Colour table can be viewed at wileyonlinelibrary.com]

Before dye extraction	After dye extraction	After grinding
		

the adsorbents by using Langmuir and Freundlich isotherm models.

The maximum adsorption capacities (q_{max}) and the K_L constants were calculated from the slope and interception of the Langmuir plots by using the equation [12]

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L C_e} + \frac{1}{q_{max}}\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

where q_e (mg g^{-1}) is the amount of MG adsorbed per unit mass of adsorbent particles at equilibrium, C_e (mg l^{-1}) is the equilibrium liquid concentration of MG, K_L is the equilibrium constant (l mg^{-1}), and q_{max} is the amount of adsorbate required to form the monolayer (mg g^{-1}) [12].

The Freundlich constants n and K_f were calculated from the slope and interception of the Freundlich plots by using the equation [13]

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (4)$$

where K_f and n are constants incorporating all factors affecting the adsorption process, such as adsorption capacity and intensity respectively.

As the evaluation of time is essential in order to obtain vital information on how fast the adsorption process reaches equilibrium [14], the kinetics of MG adsorption on the nutshell was also analysed using pseudo-first-order and pseudo-second-order kinetics.

Results and Discussion

Results related to the use of nutshell as a natural dye

Washing and rubbing fastness values of dyed samples are listed in Table 3.

From Table 3 it can be seen that, in the case of mordant usage in the dyeing process, washing fastness values do not change because the nutshell's washing fastness value is already good and the colours obtained are pale shades (see Table 4). However, it can be said that mordant (especially ferrous sulphate) usage has a negative effect on both dry and wet rubbing fastness values. The reason for this is thought to be the increase in the amounts of dye bonded onto the fibre surface. These dye molecules on the fibre surface will pass through the test fabric during the rubbing fastness test.

CIE $L^*a^*b^*$ and K/S values of dyed samples are given in Table 4. As can be seen from Table 4, mordant usage affected both the lightness-darkness (L^*) value and nuance (a^* and b^* values) of the colour. In the case of mordant usage in dyeing, the L^* value decreases and the colour yield (K/S) increases. These results indicate that colour gets darker. However, the most important change occurs in a^* and b^* values of the colour. This means the colour nuance completely changed. As can be seen from Figure 3, especially in the presence of ferrous sulphate, colour turns from reddish to greenish. As generally known, in the case of mordant usage, coordinate covalent bonds are formed between the dye molecule and fibre, and this complex formation is the possible reason for colour changes. This feature of mordants is used to obtain various colours using the same dye.

Table 4 CIE $L^*a^*b^*$ and K/S values of dyed samples with extract solution of nutshell

Material	Mordant type	L^*	a^*	b^*	C^*	h	K/S
Cotton		81.0	5.9	10.0	11.6	59.4	2.2
	$KAl(SO_4)_2$	73.4	6.3	13.2	14.6	64.5	2.0
	$FeSO_4$	65.3	2.4	15.7	15.9	81.2	4.1
Wool		68.5	7.6	14.5	16.3	62.3	0.6
	$KAl(SO_4)_2$	75.8	5.1	18.6	19.3	74.8	1.1
	$FeSO_4$	61.1	1.7	12.9	13.0	82.5	3.5

Results related to the use of nutshell as a natural adsorbent

The removal efficiencies of MG by nutshell at different contact times are shown in Figure 4. As can be seen from Figure 4, the adsorption capacity of MG increases with contact time and reaches equilibrium in 120 min. At the initial stage, fast adsorption occurs because of the large number of surface sites available for adsorption [6].

The removal efficiencies of MG by nutshell at different adsorbent doses are shown in Figure 5. As can be seen from Figure 5, the colour removal efficiency of MG increases from 48% to 98% as the adsorbent dose increases from 0.2 to 2.4 g l^{-1} at 7 mg l^{-1} initial dye concentration with an equilibrium time of 120 min. As is known, adsorption increases with increase in adsorbent dose because of the increase in the number of available adsorption sites and the surface area [15].

Adsorption isotherms were also studied in order to describe the interaction between adsorbent and MG dye. To this end, the most widely used Langmuir and Freundlich isotherm equations were employed. Figure 6 shows non-linear modelling of adsorption of MG by nutshell, and Figure 7 shows the linear Langmuir plot. The linear plot of the Freundlich isotherm is not shown because of the lower R^2 value (0.91) than in the case of the Langmuir isotherm.

Table 3 Fastness values of dyed samples with nutshell

		Washing fastness						Rubbing fastness	
Material	Mordant type	WO	PAC	PES	PA	CO	CA	Dry	Wet
Cotton		5	5	5	5	5	5	5	4–5
	$KAl(SO_4)_2$	5	5	5	5	5	5	5	4
	$FeSO_4$	5	5	5	5	5	5	4–5	3
Wool		5	5	5	5	5	5	5	4
	$KAl(SO_4)_2$	5	5	5	5	5	5	4–5	3–4
	$FeSO_4$	5	5	5	5	5	5	3–4	3–4

Figure 3 Colours obtained on cotton and wool by using nutshell as a natural dye [Colour figure can be viewed at wileyonlinelibrary.com]

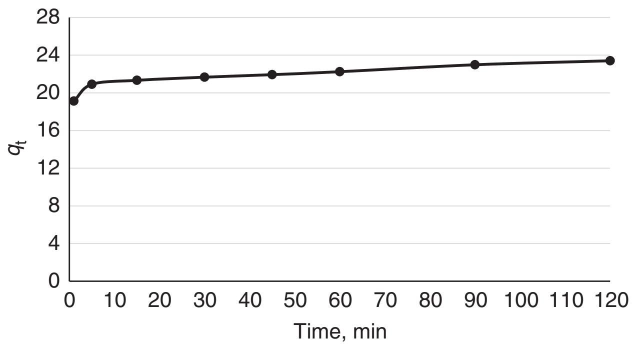


Figure 4 Effect of time on MG adsorption (adsorbent dose 0.8 g l^{-1}, initial concentration 20 mg l^{-1})

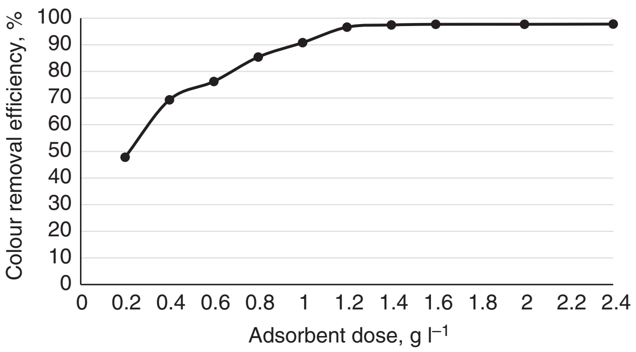


Figure 5 Effect of adsorbent doses on MG adsorption (initial dye concentration 7 mg l^{-1}, equilibrium time 120 min)

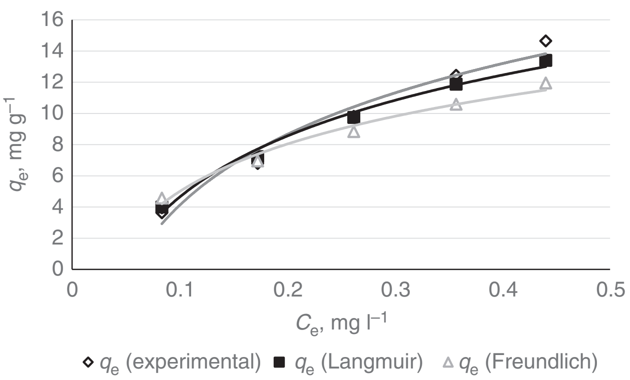


Figure 6 Non-linear isotherm modelling of adsorption of MG by nutshell

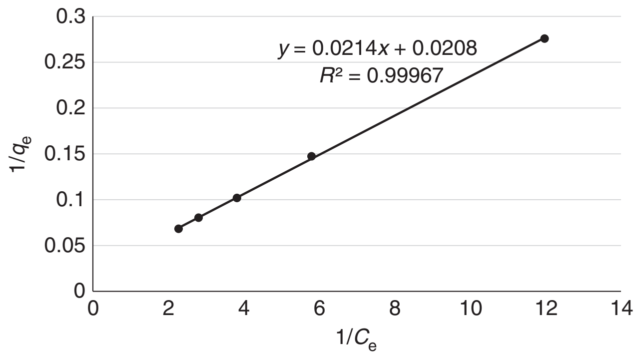


Figure 7 Linear Langmuir isotherm plots for the adsorption of MG on nutshell

As can be seen from Figure 6, experimental values of q_e and calculated values of q_e by the Langmuir isotherm model are very close to each other. As is known, a relatively high correlation coefficient value indicates that the model successfully describes the isotherm. The R^2 value of the Langmuir model, which is based on monolayer, uniform, and finite adsorption site assumptions [16], shows that it represents the experimental data well. The characteristics of the Langmuir isotherm could be expressed by a separation factor, R_L, which is defined by McKay *et al.* [17] as

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The R_L values indicate the type of isotherm. Favourable adsorption is indicated by $0 < R_L < 1$. In this study, the Langmuir isotherm constants were found to be $q_{max} = 48$ mg g^{-1} and $K_L = 1.03$ l mg^{-1} for MG adsorption on nutshell. The R_L values were found to be between 0.07 and 0.24 for initial dye concentrations of 3–12 mg l^{-1}. So, favourable adsorption is indicated for MG adsorption on nutshell.

Table 5 gives the q_{max} values for MG adsorption on nutshell obtained in this study in comparison with the q_{max} values obtained in other studies carried out with various adsorbents.

As can be seen from Table 5, the maximum adsorption capacity (q_{max}) of nutshell has a value of 48 mg g^{-1} for adsorption of MG on nutshell. When the adsorption capacity of nutshell is compared with other adsorbents, it can be understood that it possesses fairly good adsorption

Table 5 Adsorption capacities obtained from this study and other studies for the removal of MG

Adsorbents	Adsorption capacity, mg g^{-1}	References
Nutshell	48	Present study
Coconut coir AC	27.44	[1]
Sugar cane dust	4.88	[18]
Iron humate	19.2	[19]
Rice husk	76.92	[20]
AC commercial grade	8.27	[21]
Waste apricot	116.27	[22]
Lemon peel	51.73	[23]
Activated carbon	149	[24]
Hen feathers	26.1	[25]

capacity for MG dye. Although it has approximately five times lower capacity compared with activated carbon, which is the most frequently used adsorbent, it is still advantageous in terms of cost even if it is used five times more than activated carbon. Furthermore, a waste could be used, which is a very important issue in today's circumstances in terms of environmental ecology. From these results it can be said that nutshell could be used as a low-cost adsorbent to remove MG from aqueous solution.

As the evaluation of time is essential in order to obtain vital information on how fast the adsorption process reaches equilibrium [14], the kinetics of MG adsorption on nutshell was also analysed using pseudo-first-order and pseudo-second-order kinetics. Figure 8 gives non-linear plots of experimental values of q_t and calculated values of q_t by pseudo-first-order and pseudo-second-order equations, and Figure 9 gives the plot of the pseudo-second-order equation for adsorption of MG on nutshell for an initial concentration of 20 mg l^{-1} MG. The R^2 of the pseudo-first-order equation was 0.929, which was lower than the pseudo-second-order kinetic model. For this reason, results related to the pseudo-first-order equation are not shown. Owing to the increase in the driving force at higher concentration, the rate of adsorption increases with increasing initial MG concentration [26].

From the R^2 value (0.999) given in Figure 9 it can be considered that the adsorption kinetics of MG on nutshell fits the pseudo-second-order kinetic model well for an initial concentration of 20 mg l^{-1}. According to Azizian [27], when the initial concentration of the solution (C_0) is high, its sorption kinetics fits the pseudo-first-order model

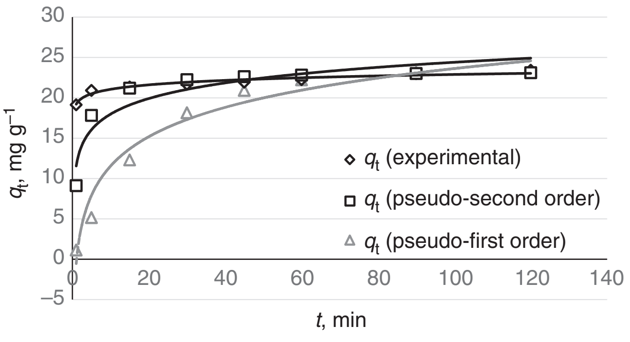


Figure 8 Non-linear plots of kinetic models for adsorption of MG on nutshell (C_0 = 20 mg l^{-1})

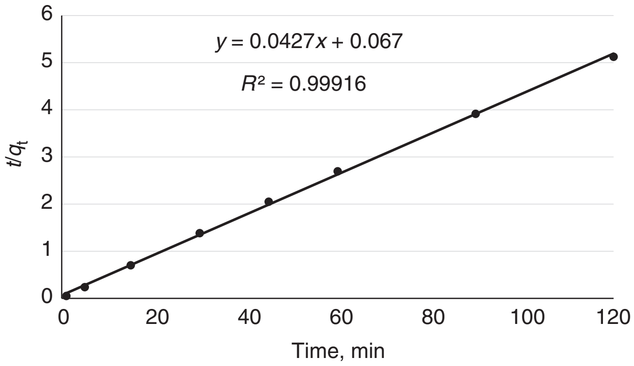


Figure 9 Linear plot of the pseudo-second-order equation for adsorption of MG on nutshell (C_0 = 20 mg l^{-1})

Table 6 Effect of initial concentration on R^2 of the pseudo-first-order (R_1^2) and pseudo-second-order (R_2^2) models

Dye	Adsorbent	C_0 (mg l^{-1})	R_1^2	R_2^2	References
AB25	Peat	20	0.907	0.999	[28]
AB25	Peat	200	0.972	0.924	[28]
AB25	Wood	20	0.978	0.996	[29]
AB25	Wood	200	0.998	0.917	[29]
MG	Nutshell	20	0.929	0.999	Present study
MG	Nutshell	50	0.990	0.841	Present study

better, while it obeys the pseudo-second-order kinetics model at a lower initial concentration of the solute. Table 6 gives the effect of the initial concentration for the present study and that obtained in other studies [26].

As can be seen from Table 6, R^2 of the pseudo-second-order model decreases from 0.999 to 0.841 and R^2 of the pseudo-first-order model increases from 0.929 to 0.990 when the C_0 increases from 20 to 50 mg l^{-1} in our study.

Conclusions

In this study it was determined that cotton and wool fabrics can be uniformly dyed with high washing and rubbing fastnesses by using nutshell as a natural dye even without mordant usage. This is a very important point in terms of industrial applications because mordant usage, which causes environmental pollution, is avoided. Taking into consideration that the most important problem in dyeing with natural dyes is low fastness values, it can be said that nutshell, which gives good wet fastness values without the requirement of mordant usage, could be a good alternative for dyeing cotton and wool fabrics with natural dyes.

In this study, nutshell was also used as an adsorbent for MG removal after extracting its dye. The influence of agitation time and adsorbent dose on the removal of MG in aqueous solution by nutshell was evaluated. The amount of dye adsorbed increased with increase in agitation time, and it achieved equilibrium at 120 min. Adsorption equilibrium studies were used to determine the adsorption capacity of the adsorbent by using Langmuir and Freundlich isotherm models. Equilibrium data were described well by the Langmuir model. Kinetic data fitted the pseudo-second-order kinetic model well for low initial dye concentrations.

All these results indicate that nutshell, which is a waste, could be used as a low-cost adsorbent to remove MG from aqueous solution. The advantage of nutshell usage as an adsorbent for colour removal is its low cost.

By taking all results found in this study into consideration, it can be concluded that nutshell can be used firstly as a natural dye for ecological dyeing of cotton and wool fabrics and then as a natural adsorbent for colour removal of basic dye effluent.

References

1. U S Banerjee and Y C Sharma, *J. Ind. Eng. Chem.*, **19** (2013) 1099.
2. P Sathishkumar, M Arulkumar and T Palvannan, *J. Clean. Prod.*, **22** (2012) 67.
3. L Wang, *J. Environ. Manag.*, **102** (2012) 79.
4. P Janos, P Sedivy, M Ryznarova and S Grötschelova, *Chemosphere*, **59** (2005) 881.
5. A Demirbaş, *J. Hazard. Mater.*, **167** (2009) 1.
6. M N Idris, Z A Ahmad and M A Ahmad, *Int. J. Basic Appl. Sci.*, **11** (2011) 38.
7. E Güneş and R Atav, *1st Int. Conf. Natural Fibers. Book of Abstracts*, Guimarães, Portugal (2013) 115.
8. A Thakur, *J. Med. Plants Res.*, **5** (2012) 5324.
9. J N Chakraborty, *Fundamentals and Practices in Colouration of Textiles*, 2nd Edn (New Delhi: Woodhead Publishing India Pvt Ltd, 2014) 247.
10. *ISO 105-C06:2010 Textiles: Tests for colour fastness. Part C06: Colour fastness to domestic and commercial laundering* (Basel: ISO, 2010).
11. *ISO 105-X12:2016 Textiles: Tests for colour fastness. Part X12: Colour fastness to rubbing* (Basel: ISO, 2016).
12. H Aydın, Y Bulut and Ç Yerlikaya, *J. Environ. Manag.*, **87** (2008) 37.
13. H Freundlich, *J. Phys. Chem.*, **57** (1906) 385.
14. M K Dahri, M R R Kooh, B L Linda and L B L Lim, *J. Environ. Chem. Eng.*, **2** (2014) 1434.
15. R Malik, D S Ramteke and S R Wate, *Waste Manag.*, **27** (2007) 1129.
16. I Langmuir, *J. Am. Chem. Soc.*, **40** (1918) 1362.
17. G McKay, H Blair and J R Gardiner, *J. Appl. Polym. Sci.*, **28** (1989) 1499.
18. S D Khattri and M K Singh, *Indian J. Chem. Technol.*, **6** (1999) 112.
19. P Janos, *Environ. Sci. Technol.*, **37** (2003) 5792.
20. I A Rahman, B Saad, S Shaidan and E S Sya Rizal, *Bioresour. Technol.*, **96** (2005) 1578.
21. I D Mall, V C Srivastava, N K Agarwal and I M Mishra, *Colloids Surf. A: Physicochem. Eng. Asp.*, **264** (2005) 17.
22. C A Başar, *J. Hazard. Mater.*, **135** (2006) 232.
23. A Mittal, *J. Hazard. Mater.*, **133** (2006) 196.
24. Y Önal, C Akmil-Başar and C Sarıcı-Özdemir, *J. Hazard. Mater.*, **146** (2007) 194.
25. K V Kumar, *Dyes Pigm.*, **74** (2007) 595.
26. B H Hameed and M I El-Khaiary, *J. Hazard. Mater.*, **154** (2008) 237.
27. S Azizian, *J. Colloid Interface Sci.*, **276** (2004) 47.
28. Y S Ho and G McKay, *Chem. Eng. J.*, **70** (1998) 115.
29. Y S Ho and G McKay, *Process. Saf. Environ. Prot.*, **76** (1998) 183.

