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Column Studies for Removal of Acid Yellow Dye 17 from Synthetic Water Using Activated Saw Dust†

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Continuous fixed-bed studies were undertaken to evaluate the efficiency of activated saw dust powder as an adsorbent for the removal of Acid yellow 17 from aqueous solution under the effect of various process parameters like bed depth (10-20 cm), flow rate (6-10 mL/min) and initial concentrations (10-30 mg/L) of Acid yellow 17. The results showed that the total adsorbed quantities and equilibrium uptake decreased with increasing flow rate and increased with increasing inlet Acid yellow 17 concentration. The results showed that the column performed well at low flow rate. Also, breakthrough time and exhaustion time increased with increasing bed depth. Thomas model was applied to the adsorption of Acid yellow 17 at different bed depths, flow rates and inlet concentrations to predict the breakthrough curves and to determine the characteristic parameters of the column that are useful for process design. The model prediction was in good agreement with the experimental results at all the process parameters studied indicating that they were most suitable for activated saw dust column design.

Keywords: Adsorption, Acid Yellow 17, Column, Thomas model, Saw dust.

INTRODUCTION

Environmental pollution is having an adverse effect on human ecosystems. Synthetic dyes are consumed by paper, textile, leather, plastics industries, *etc*. and hence contribute as major sources of water pollutants. Dyes contain various organic and inorganic matters, which possess a threat to organisms and environment since they are toxic even at low concentrations. Acid dyes are water-soluble dyes employed mostly in the form of sodium salts of the sulfonic or carboxylic acids. They are anionic which attach strongly to cationic groups in the fibre directly [1]. They can be applicable to all kind of natural fibers like wool, cotton and silk as well as to synthetics like polyesters, acrylic and rayon. But they are not substantive to cellulosic fibers. They are also used in paints, inks, plastics and leather. It is well known that most of the acid dyes are toxic to aquatic organisms and carcinogenic to humans [2]. Therefore, in order to avoid the environmental problems effectively caused by these pollutants and their hazardous effects on living beings, it is necessary to remove these dyes from wastewater before being discharged to water bodies [3]. At present, the methods include the use of coagulation/flocculation, oxidation, photo catalytic processes, membrane technology and biological treatments. However, these processes have disadvantages and limitations, such as high cost, generation of secondary pollutants and poor removal efficiency. Thus, adsorption has been found to be an effective and attractive process for the treatment of these wastewaters [4]. Adsorbents, which are generally used for dye wastewater treatment are alumina, silica gel, activated carbon, zeolite, *etc*. An alumina is a synthetic porous crystalline gel, which is available in the form of granules of different sizes having surface area ranging from 200 to 300 m^2 g^{-1}. However, the preparation and regeneration of activated carbon adsorbents are fairly expensive, which hampers their application. Hence, a considerable amount of interest has recently been focused on the production of low-cost wastes for the removal of dyes from wastewater. Sawdust or wood dust is a by-product of cutting, grinding, drilling, sanding, or otherwise pulverizing wood with a saw or other tool. Sawdust is flammable and accumulation provides a ready source of fuel. Airborne sawdust can be ignited by sparks or even heat accumulation and result in explosions. Airborne sawdust and sawdust accumulations present a number of health and safety hazards. Saw dust becomes a potential health problem when, for example, the wood particles, from processes such as sanding, become airborne and are inhaled. Wood dust is a known human carcinogen. Certain woods and their dust contain toxins that can produce severe allergic reactions [5].

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Adsorption process may be carried out in batch contactors such as agitated vessels for the treatment of small volume of effluents, but are less convenient to be used on industrial scale, where large volumes of wastewater are continuously generated. Fixed bed systems are advantageous for continuous treatment of wastewater containing dyes, as these contactors do not need the movement of solids or separation of solids from suspensions after treatment. There are few studies reported on the use of activated saw dust in fixed bed column for adsorption of pollutants from water. The studies on systematic approach on efficiency of saw dust for removal of dye from dye aqueous solutions and detailed column studies for dye removal process using activated saw dust are scarce. Thus, in present study, adsorption of Acid yellow 17, an acidic dye on saw dust has been investigated in fixed bed continuous column. Breakthrough studies are carried out to evaluate the performance of saw dust in continuous fixed-bed operation by varying the operating conditions, such as the flow rate, bed depth and influent Acid yellow 17 concentration. Thomas model has been used to analyze the breakthrough curve for the adsorption of Acid yellow 17.

EXPERIMENTAL

The raw sawdust was collected from the local saw mill and sieved through a mesh of size 0.5 mm. The sawdust was sun dried, then oven dried at 100 °C until properly dried, then treated with 2 N H_2SO_4 acid *i.e.* 100 g of dry sawdust in 500 mL of H_2SO_4 for 3 h, then excess amount of acid was decanted. The remaining sample was washed with distilled water to remove the surface acidity and dried at 90-100 °C in an oven. After drying keep the sample in a furnace for activation at 600 °C for 2 h. The sample was ground and sieved with a 150 μm mesh sieve. The activated sawdust having less than 150 μm size were collected and stored in airtight container. A proper ratio of 1:2 activated saw dust and cement was mixed properly with required quantity of water to form paste such that its pellets are made of diameter 0.5 cm and length 1 cm. All working solutions were prepared by diluting the stock solution with distilled water to the desired concentration.

Effect of pH: The solution of Acid yellow dye 17 with initial concentration of 20 mg/L was taken in different conical flasks. The initial solution pH was maintained for different pH ranging from 2 to 12 using 0.1 N HCl and 0.1 N NaOH. A dosage of 0.1 g of activated saw dust was added to all the flasks and kept for shaking for the duration of 45 min in incubating shaker at 100 rpm. The contents were centrifuged and the remaining concentration of dye was measured from calibration graph. A plot of percentage adsorption against pH was obtained.

Experimental set up for column studies: Continuous flow sorption experiments were conducted in a glass column (3 cm internal diameter and 30 cm height). A known quantity of activated saw dust pellets were placed in the column to yield the desired bed height of the sorbent. Acid yellow 17 solution with known inlet concentration and pH was pumped upwards through the column at a desired flow rate. Samples were collected from the top of the column at different time intervals and were analyzed for Acid yellow 17 using a UV/visible spectrometry (Labtronics LT-2700) by monitoring the absorbance changes at a wavelength of maximum absorbance 662 nm.

Analysis of column data: The time for breakthrough appearance and shape of the breakthrough curves are important characteristics for determining the operation and the dynamic behaviour of an adsorption column. The breakthrough time (t_b, the time at which dye concentration in the effluent reached 0.5 % of inlet dye concentration) and bed exhaustion time (t_e, the time at which dye concentration in the effluent reached 99.5 % of influent dye concentration) were used to evaluate the breakthrough curves. The break through curves were generated for various conditions of flow rate, influent concentration of dye and bed height. The total adsorbed dye (q_{total}), equilibrium uptake (q_b), total amount of dye entering column (M_{Total}), % adsorption were calculated from equations from 1 to 3 respectively.

The total adsorbed dye from single dye solution was calculated from eqn. 1:

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_d dt \quad (1)$$

q_{total} can be obtained by area above the breakthrough curve C *vs*. t, where C is the concentration of dye removed in mg/L. C_d is the total adsorbed concentration of dye. Q is the flow rate of dye solution, mL/min. t_{total} is the totals time taken for adsorption studies in fixed bed column.

Equilibrium uptake q_e (mg/g) or maximum capacity of the column was calculated by eqn. 2:

$$q_e = \frac{q_{total}}{M} \quad (2)$$

where M, is the mass of adsorbent in column. Total amount of dye entering column (M_{Total}) was calculated by eqn. 3:

$$M_{Total} = \frac{QC_o t_{total}}{1000} \quad (3)$$

where t_{total}, is the total time for the adsorption in the column.

Modelling of column data: Thomas model presented in eqn. 4 is simple and widely used by several investigators to describe the prediction of the concentration time profile or breakthrough curve for the dyes in packed bed sorption system. Thomas model is based on second-order reaction kinetics and the assumption of non-linear equilibrium relationship of Langmuir isotherm. Thomas model neglects the axial dispersion [6] and assumes plug flow behaviour in the bed. This model is employed by many researchers to predict the break through curves for adsorption of dyes [6-9]. The column sorption data obtained at different bed heights, flow rates and dye concentrations can be fitted using Thomas model. Thomas model is given in eqn. 4:

$$\frac{C}{C_o} = \frac{1}{1+\exp\left(\frac{K_{Th}}{F}(q_t M - C_o t)\right)} \quad (4)$$

where C is effluent concentration of dye, C_o is influent concentration of dye, K_{Th} is Thomas model rate constant (mL/min g), q_t is maximum solid phase concentration of solute (mg/g), t is the time, min, M is mass of the adsorbent (g) and F is flow rate (mL/min).

The linearized form of the Thomas model is expressed as follows:

$$\ln\left(\frac{C_o}{C}-1\right)=\frac{K_{Th}q_tM}{F}-K_{Th}C_ot \quad (5)$$

Kinetic coefficient K_{Th} and adsorption capacity q_t can be determined by plotting the graph of $\ln\left(\frac{C_o}{C}-1\right)$ *vs.* t at a given conditions.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on percentage adsorption of Acid yellow dye 17 was studied in batch operation by varying the initial pH of dye solution from 2 to 10 with constant dosage of 0.1 g/L and initial concentration of 20 mg/L. From, Fig. 1, it can be observed that percentage adsorption was more at lower pH of 2 and decreased with increase in pH. Low pH was found to be favourable for maximum adsorption of Acid yellow 17. Similar results were also reported for the removal of Acid yellow 36 onto activated carbons prepared from saw dust and rice husk [10]. Two possible mechanisms of adsorption of Acid yellow 17 on activated saw dust may be electrostatic interaction between the protonated groups of carbon and acidic dye. At low pH, significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic acid dye. As the pH of the system increases the number of negatively charged sites increases and the number of positively charged surface site decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to electrostatic repulsion.

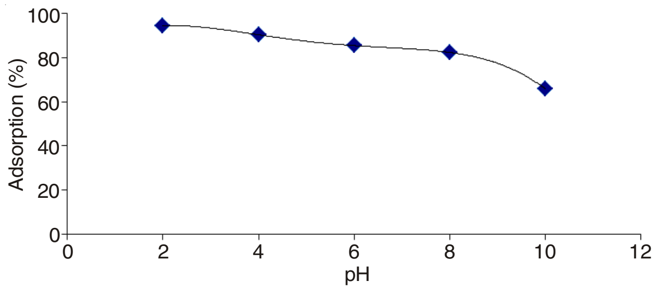

Fig. 1. Effect of pH on percentage adsorption of Acid yellow 17 (initial concentration of dye 20 mg/L, dosage 0.1 g/L)

Effect of inlet concentration of dye: The adsorption performance of saw dust was tested at various Acid yellow 17 inlet concentrations. The sorption breakthrough curves obtained by changing inlet Acid yellow 17 concentration from 10 to 30 mg/L at 6 mL/min flow rate and 10 cm bed height are given in Fig. 2. As expected, a decreased inlet concentration gave a later breakthrough curve and the treated volume was greatest at the lowest inlet concentration since the lower concentration gradient caused a slower transport due to a decreased diffusion coefficient or decreased mass transfer coefficient. The breakthrough time decreased with increasing inlet Acid yellow 17 concentration as the binding sites became more quickly saturated in the column. Breakthrough time occurred at 13.5 h for 10 mg/L Acid yellow 17 inlet concentration while as breakthrough time occurred at 2.4 h at an inlet Acid yellow 17 concentration of 30 mg/L. The total adsorbed Acid yellow 17 quantities, equilibrium Acid yellow 17 uptake, break through time, exhaustion time, at different initial Acid yellow 17 concentrations are shown in Table-1. The maximum adsorption capacity of saw dust was 4.34 mg/g at an inlet Acid yellow 17 concentration of 10 mg/L. At lower inlet dye concentrations, the competition for adsorption was less, accordingly, higher uptake were obtained. Similar observations of decrease in dye uptake with increase in influent concentration was reported by Uddin *et al.* [11] for adsorption of Reactive black on granular activated carbon.

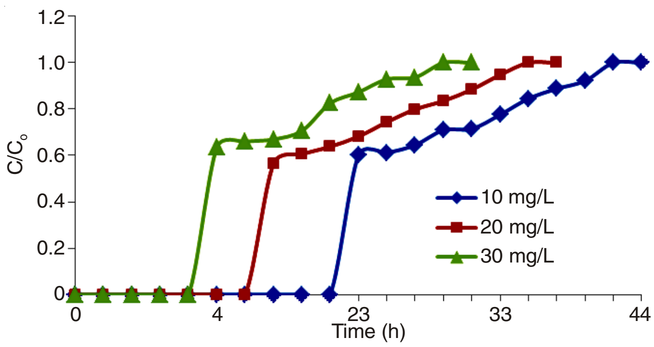

Fig. 2. Break through curve for effect of inlet concentration (flow rate = 6 mL/min, bed height = 10 cm)

TABLE-1
EFFECT OF BED HEIGHT, FLOW RATE AND INLET CONCENTRATION ON BED CAPACITY, BREAK THROUGH TIME AND EXHAUSTION TIME

Bed height (cm)	Flow rate (mL/min)	Inlet conc. (mg/L)	t_b (h)	t_e (h)	q_{total} (mg)	q_e (mg/g)
10	6	20	6.5	30.5	99	4.15
15	6	20	13.5	44	198	5.53
20	6	20	22.5	67	279	5.85
10	6	20	6.5	30.5	99	4.15
10	8	20	4.1	27.5	81	3.39
10	10	20	2.1	24	63	2.64
10	6	10	13.5	36.5	103.5	4.34
10	6	20	6.5	30.5	99	4.15
10	6	30	2.2	23	90	3.77

Effect of flow rate: The effect of flow rate on Acid yellow 17 adsorption by saw dust was investigated by varying the flow rate from 6 to 10 mL/min and keeping the initial Acid yellow 17 concentration (20 mg/L) and bed depth (10 cm) constant. The plot of normalized Acid yellow 17 concentration *versus* time at various flow rates is shown in Fig. 3. The break through curve becomes steeper when the flow rate is increased with which the breakthrough point time and adsorbed Acid yellow 17 concentration decreases. This may be because the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the Acid yellow 17 solution leaves the column before equilibrium occurs. Thus, the contact time of Acid yellow 17 with saw dust is very short at higher flow rate resulting decrease in uptake capacity. The results obtained in the present investigation are in agreement with the results obtained by other researchers [9,11] on continuous dye adsorption by different adsorbents in fixed bed column. The decrease in adsorption capacity with increase in flow rate may be due to shorter residence time of

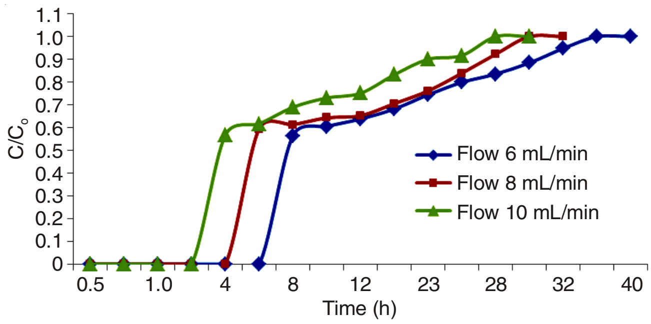

Fig. 3. Break through curve for effect of flow rate (concentration = 20 mg/L, bed height = 10 cm)

the adsorbate molecule in the fixed bed column. At higher flow rates enough time will not be available for the dye molecules to diffuse through the pores to occupy the active sites available at the interior pore surfaces.

Effect of bed height: The sorption breakthrough curves obtained by varying the bed heights from 10 to 15 cm at 6 mL/min flow rate and 20 mg/L inlet Acid yellow 17 concentration for saw dust are presented in Fig. 4. The bed capacity, break through time (t_b) and exhaustion time (t_e) were increased with increasing bed height, as more binding sites were available for sorption. The increase in adsorption with bed depth was due to the increase in adsorbent doses in larger beds, which provide greater adsorption sites for Acid yellow 17. The total adsorbed Acid yellow 17 quantities, equilibrium Acid yellow 17 uptake obtained from the column data.

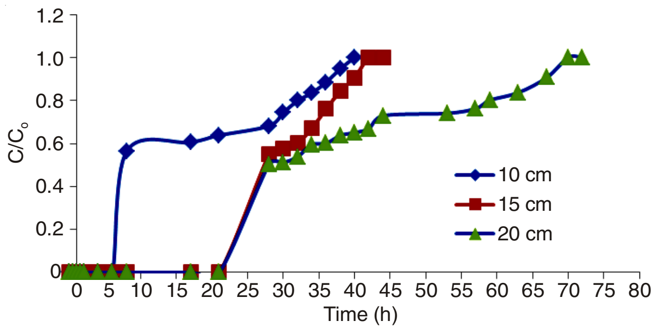

Fig. 4. Break through curve for effect of bed height (inlet concentration = 20 mg/L, flow rate = 6 mL/min)

Increase in dye uptake with an increase in bed height has been also reported by Malik [9] in adsorption of Reactive black on activated carbon and anionic Reactive red 24 on activated carbon prepared from sewage sludge. Increase in dye uptake with increase in bed height can be attributed to availability more effective surface area of adsorbent which offers increased availability of active binding sites for adsorption because of larger mass of saw dust pellets.

From the above results, it can be summarized that, lower flow rate, increased bed height and lower inlet concentration results in delayed breakthrough, higher uptake, thus leading to effective operation of continuous adsorption and efficient use of activated saw dust pellets in fixed bed column for adsorption of Acid yellow 17 from dye solution.

Application of Thomas model: Thomas model was fitted to the column data to investigate the breakthrough behaviour of Acid yellow 17 onto activated saw dust. The eqn. 5 was tested for its validity using the breakthrough curve data obtained for Acid yellow 17 at various bed heights, flow rates and inlet concentrations by plotting $\ln\left(\frac{C_o}{C}-1\right)$ *vs.* t for Thomas model. Validity of the model was determined through the linear nature of the plots and the goodness of fit was analyzed through the values of coefficient of determination (R^2). The values of the constants or parameters (K_{Th} and q_t) were obtained from the slope and intercept of the plots.

The plots $\ln\left(\frac{C_o}{C}-1\right)$ *vs.* t for Acid yellow 17 at different bed height, flow rates and influent concentrations are presented in Figs. 5-7, respectively. The high coefficient of determination ($R^2 > 0.90$) obtained by fitting the data onto Thomas model suggests that the Thomas model is suitable for describing the column adsorption data for Acid yellow 17 adsorption on activated saw dust pellets from single dye aqueous solution, thus proving the validity of the model for continuous dye adsorption in fixed bed column involving dye-adsorbent system. Thomas model parameters calculated for dyes at various bed heights, flow rates and influent concentrations are presented in Table-2.

From Table-2, it can be seen that as the bed depth increases for dye, the K_{Th} decreased whereas, q_t values increased. The increase in q_t values may be due to higher adsorption binding sites available with higher bed height in the column, which increases the bed capacity q_t. From Table-2, it can be seen that with the increase in flow rate of dye solution, K_{Th} increased whereas, q_t values decreased. At a very high flow rate, owing to lower residence time, the time available for achievement of adsorption equilibrium reduced, resulting in lower adsorption capacity q_t.

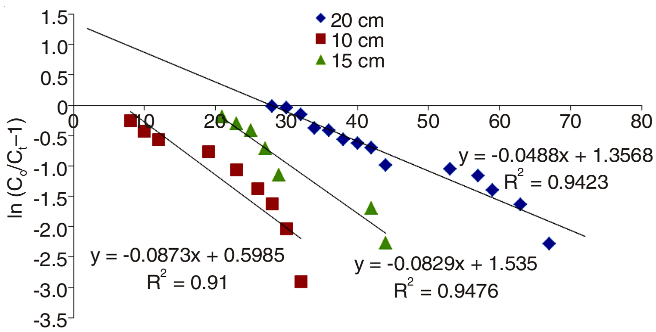

Fig. 5. Thomas model validation for Acid yellow 17 adsorption on pellets at different bed height

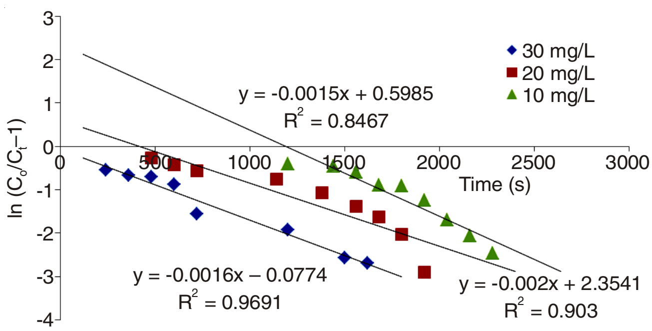

Fig. 6. Thomas model validation for Acid yellow 17 adsorption on pellets at different flow rates

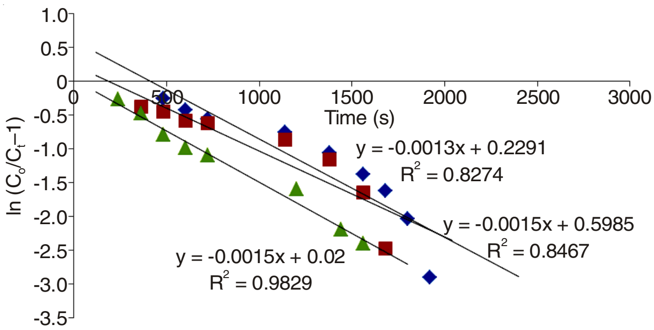

Fig. 7. Thomas model validation for Acid yellow 17 adsorption on pellets at different inlet concentrations

TABLE-2
THOMAS MODEL PARAMETERS AT DIFFERENT INITIAL DYE CONCENTRATIONS (ppm), FLOW RATE (mL/min), BED HEIGHT (cm)

Inlet dye conc. (mg/L)	Flow rate (mL/min)	Bed height (cm)	K_{Th} (mL/mg min)	q_t (mg/g)
10	6	10	0.2	2.959
20	6	10	0.08	1.807
30	6	10	0.05	0.364
10	8	10	0.07	1.181
10	10	10	0.75	0.111
10	6	15	0.07	3.676
10	6	20	0.04	4.234

From Table-2, it can be observed that with the increase in influent concentrations of dye, the K_{Th} values increased and q_t values decreased. The value of q_t decreased with increase in influent concentration. It can be attributed to the faster rate of adsorption of dye molecules on to the active sites on the exterior surface of the pellets due to larger driving force for adsorption. Such a phenomena would lead to non-utilization of all the active sites in the saw dust pellets, leading to lower q_t at higher influent concentrations. It may also be due to higher number of dye molecules competing for limited active sites.

Thus the lower flow rate, lower inlet concentration of dye and higher bed depth would increase the adsorption of Acid yellow 17 on the activated saw dust containing column. The variation of K_{Th} with increase in bed height, increase in flow rate and inlet concentration of dye solution shows that external mass transfer and/or internal diffusion may be playing a role in the packed bed adsorption process and the assumption of Thomas model, which states the absence of these resistances, is not truly valid for the present situation.

Conclusion

The adsorption studies for continuous removal of Acid yellow dye 17 has been studied in fixed bed column using activated saw dust pellets. The present study showed that adsorption of Acid yellow dye 17 from synthetic water is feasible with activated saw dust in fixed bed continuous column adsorption system. It was found that the maximum percentage adsorption was found at 2 pH (acidic condition) in batch studies. The dye uptakes in fixed bed column were found to be high at lower flow rate, lower concentrations and higher bed height. Thomas model was found adequate to describe breakthrough behaviour of the adsorption process which had optimum conditions at high bed depth (20 cm), low influent concentration (10 mg/L) and flow rates (6 mL/min). The coefficients were determined from the slope and intercepts obtained from the linear regression performed on each set of transformed data. Analysis of regression coefficients indicated that the regressed lines provided excellent fits to the experimental data with high R^2 values. The bed capacity q_t decreased and the coefficient K_{Th} increased with increasing flow rates. On the other hand, with increase in the initial dye concentration, bed height, the values of q_t increased and that of K_{Th} decreased.

REFERENCES

1. H. Zollinger, Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, VCH Publishers, New York, edn 2 (1991).
2. F.P. van der Zee and S. Villaverde, *Water Res.*, **39**, 1425 (2005).
3. M.N. Rashed, Organic Pollutants - Monitoring, Risk and Treatment, INTECH (2013).
4. A.E. Nemr, O. Abdelwahab, A. El-Sikaily and A. Khaled, *J. Hazard. Mater.*, **161**, 102 (2009).
5. K.H. Chu, *J. Hazard. Mater.*, **177**, 1006 (2010).
6. F. Han, V.S.R. Kambala, M. Srinivasan, D. Rajarathnam and R. Naidu, *Appl. Catal. A*, **359**, 25 (2009).
7. K. Vijayaraghavan and Y.S. Yun, *Biotechnol. Adv.*, **26**, 266 (2008).
8. A.A. Ahmad and B.H. Hameed, *J. Hazard. Mater.*, **175**, 298 (2010).
9. P.K. Malik, *Dyes Pigments*, **56**, 239 (2003).
10. Z. Zulfadhly, M.D. Mashitah and S. Bhatia, *Environ. Pollut.*, **112**, 463 (2001).
11. M.T. Uddin, M.A. Islam, S. Mahmud and M. Rukanuzzaman, *J. Hazard. Mater.*, **164**, 53 (2009).