



2013 International Symposium on Environmental Science and Technology (2013 ISEST)

## Adsorption and removal of acid red 3R from aqueous solution using flocculent humic acid isolated from lignite

Duanping Xu\*, Changjian Gu, Xiao Chen

*School of Resource and Environmental Engineering, Liaoning Technical University, Fuxin 123000, China*

### Abstract

Humic acid (HA) was isolated from lignite. Flocculent HA was made and used to adsorb and remove dye acid red 3R from aqueous solution. The adsorption experiments were carried out in a batch process to observe the effect of various parameters such as contact time, dose of flocculent HA, ionic strength (NaCl) as well as adsorption kinetics and isotherm. Results showed that adsorption of acid red 3R on flocculent HA could reach equilibrium at less than 180 min. The adsorption kinetics obeyed the pseudo-second order model ( $R^2=0.994$ ). The adsorption was described with Freundlich equation on the basis of value of regression coefficient ( $R^2=0.984$ ). The removal rate of the dye increased with the increase of the dose of flocculent HA, while it decreased with the addition of NaCl in the aqueous solution. These suggested that the adsorption mechanism was the electrostatic attraction, to form hydrogen bonds, and van der Waals' force between molecules of HA and acid red 3R. Conclusion was made that flocculent HA isolated from lignite could be used as an adsorbent to remove the dye from aqueous solution.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](#).  
Selection and peer-review under responsibility of Beijing Institute of Technology.

**Keywords:** Dye; Acid red 3R; Adsorption; Humic acid; Lignite

### 1. Introduction

Dyes are commonly used in many industries, such as food, paper, rubber, plastics, and textile [1]. It is estimated to be more than 100,000 commercially available dyes with over  $7 \times 10^5$  tons of dye-stuff produced annually [2]. The presence of the dye component in the discharge not only increases the overall loading of chemical oxygen demand (COD) to the receiving water but also creates an aesthetic nuisance to the environment even when the concentration is as low as 1 mg/L [3]. Moreover, several commonly can be used to remove different types of dyes from aqueous solution [5-7]. Suitable adsorbents include activated carbon [8], peat [9], chitin [10], silica [11], and others [12-14]. However, adsorption with these

\* Corresponding author. Tel.: +86-04183-352505; fax: +86-0418-3352505.  
E-mail address: [xdp1961@sina.com](mailto:xdp1961@sina.com).

adsorbents presents the disadvantage of generating a large volume of sludge. This sludge is rich in dyes, as well as other substances used in the textile process, must be discarded properly to avoid generating second contamination [15]. On the other hand, the regeneration of these adsorbents is difficult.

Humic acid (HA) is a principal component of humic substances which are the major organic constituents of soil, peat, lignite [16]. It is a complex mixture of many different acids containing aromatic rings and aliphatic chains which carry carboxyl, phenolate groups and other O-, N- and S-containing functional groups. Due to having a group of polar groups and non-polar fragments, HA can interact with metal ions, minerals and organic compounds.

In previous articles, adsorption of environmental pollutants on condensed or dissolved HA isolated from soil was investigated [17-18]. Usually the purpose of their work was to reveal the transportation or fate of contaminants in environmental media. In this paper, flocculent HA isolated from lignite was used as an adsorbent to remove dye (acid red 3R) from aqueous solution. Because of having larger surface area, flocculent HA has strong adsorption capacity. On the other hand, the sludge with HA and dyes can be used as fuel directly and no second contamination will be generated.

### Nomenclature

q	specific adsorbed amount of acid red 3R (mg/g)
$C_0$	initial concentrations of acid red 3R (mg/L)
$C_i$	equilibrium concentrations of acid red 3R (mg/L)
m	weight of HA added (g)
$q_e$	amounts of dye adsorbed on HA (mg/g) at equilibrium
$q_t$	amounts of dye adsorbed on HA (mg/g) at time t
$k_1$	rate constant of pseudo-first-order adsorption ( $\text{min}^{-1}$ ).
$k_2$	rate constant of pseudo-second-order adsorption (g/mg min).

## 2. Material and methods

### 2.1. Dye

Dye acid red 3R is purchased from Tianjing dyes factory in China and its chemical structure is presented in Fig. 1.

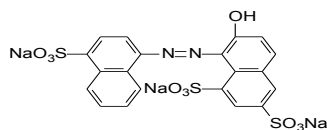


Fig. 1. Chemical structure of acid red 3R.

### 2.2. Extraction and purification of lignite HA

Lignite was collected from Huolinhe Coal Mining Company (Inner Mongolian Autonomous Region,

Northwest China), and then it was air-dried, pulverized and sieved with a 120-mesh sieve. The extraction and purification of HA was performed according to NAGOYA method [19]. Briefly, 1.0 kg of lignite sample was added to a flask with 10 L of 0.05 M HCl. The flask was intermittently shaken at 25°C for 18 h. Subsequently, the lignite was separated from water by centrifugation at  $3,000 \times g$  for 20 min, and it was washed twice with distilled water. The lignite was added with 10 L of 0.1 M NaOH solution, and then it was intermittently shaken at 25°C for 18 hours supplemented with  $N_2$ . The supernatant was collected from the lignite residue by centrifugation at  $3,000 \times g$  for 20 min and transferred to a glass beaker. The basification and separation process was repeated until a light brown color of supernatant was observed. In order to separate HA from fulvic acid (under the condition of acidity, HA will deposit while fulvic acid will not), all the supernatant was collected and acidified to pH 1-1.5 with 6 M HCl. The HA precipitate was added with 1 L of HF-HCl solution (0.1 M HF/0.1 M HCl) and shaken at 25°C for 2 h. The mixture was then separated by centrifugation at  $3,000 \times g$  for 20 min, and the supernatant with silicate was removed. The process was repeated three times, and HA with little ash was obtained. Finally, cation exchange resin was used to remove ions, and the purified HA was freezing-dried, ground to fine powder for adsorption experiments.

### 2.3. Adsorption experiments

The adsorption experiments were carried out in a batch process by using aqueous solution of dye acid red 3R with flocculent HA to observe the effect of various parameters such as contact time, initial concentration, pH of solution, HA dose, ionic strength (NaCl). Experiment on contact time was conducted as follows. Dye solutions were prepared by dissolving acid red 3R in double distilled water to 1 g/L, and then diluted to 120 mg/L. 30 mg of HA sample and 15 mL of 0.05 M NaOH solution were added into a 100-mL glass stoppered conical flask. The flask was intermittently shaken at 25°C for 2 hours until the HA was completely dissolved. Then 10 mL of 0.1 M HCl solution was added into the flask until the dissolved HA flocculated and flocculent HA was made. Subsequently, 25 mL of acid red 3R solution at a concentration of 120 mg/L was added to the flask, and the pH=2. The flask was then shaken in the shaking table at 130 rpm and 30°C. After shaking for 30, 60, 120, 210, 300, 420, 600, 900, 1,200 and 1,440 min, flasks (three parallel samples) were taken out, respectively. The supernatant was filtrated with membrane (cellulose acetate, 0.45  $\mu m$ ), and then the filtrate was analyzed at a wavelength of 505 nm by an UV/Visible spectrometer (TU 1810 made in Puxi company, China. Error of absorbance caused by filtrating with the membrane is less than 2%). The amount of adsorbed dye was determined by the mass balance equation:

$$q = V(C_0 - C_f)/m \quad (1)$$

In the adsorption isotherm study, 25 mL of acid red 3R solution with different concentrations (from 20 mg/L to 2,000 mg/L) was mixed with 25 mL of solution containing 30 mg flocculent HA (made as the process described above), respectively. The mixtures were then shaken in the shaking table for 24 h, supernatant was filtrated with membrane, and then the filtrate was analyzed by the method described above.

The pH effect on dye removal of acid red 3R from aqueous solution was investigated in a similar way as described above at different initial pH (0.5-6, because HA could be dissolved in solution when  $pH > 7$ ). The initial concentration of dye was 60 mg/L and the amount of flocculent HA was 30 mg. The dosage effect on dye removal was evaluated with the dye at an initial concentration of 60 mg/L, pH=2, and the amount of HA added ranged from 5 to 250 mg. The ionic strength effect on the dye removal was studied with different amounts of NaCl (from 0 - 0.5 mol/L). The initial concentration of solution was 60 mg/L, the amount of flocculent HA was 30 mg and pH = 2.

### 3 Results and Discussion

#### 3.1. Effect of contact time

In order to investigate adsorption equilibrium time and adsorption kinetics model of acid red 3R on flocculent HA, the adsorption experiment was carried out as a function of contact time, and the results are shown in Fig. 2. The Figure indicates that the adsorption is quite rapid in the first 30 min ( $q_e = 23$  mg/g when  $t = 30$  min), then gradually increased with the prolongation of contact time.  $q_e = 26.9$  mg/g when  $t = 60$  min,  $q_e = 34.6$  mg/g while  $t = 120$  min. After 180 min of contact, no obvious variation in  $q_e$  is examined. Based on these results, 180 min is taken as the equilibrium time.

In physical adsorption, most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. A large number of vacant surface sites are available for adsorption during the initial stage, the occurrence of solute transfer only due to sorbate and sorbent interactions with negligible interference due to solute–solute interactions. While after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [20]. The adsorption equilibrium can reach fast, which may be caused by the huge specific surface of flocculent HA.

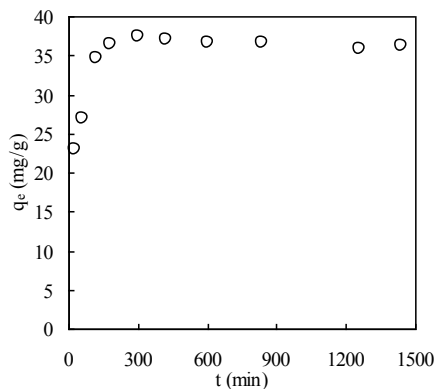


Fig. 2. Effect of contact time on adsorption of acid red 3R on flocculent HA.

#### 3.2 Adsorption kinetics

In order to investigate the mechanism of adsorption, the pseudo-first-order adsorption, and the pseudo-second order adsorption model were used to test dynamical experimental data. The pseudo-first order rate expression of Lagergren [21] is given as:

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_1}{2.303} t \quad (2)$$

The slopes and intercepts of plots of  $\log(q_e - q_t)$  vs.  $t$  were used to determine the first-order rate constant  $k_1$ . In many cases the pseudo-first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes.

The pseudo-second-order kinetic model is expressed as [22- 23]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

The slopes and intercepts of plots of  $t/q_t$  vs.  $t$  were used to calculate the second-order rate constant  $k_2$  and  $q_e$ . It is more likely to predict the behavior over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate-controlling step.

Data from Fig. 2 were regressed with Lagergren first-order and pseudo-second-order kinetics, and the results are shown in Fig. 3. The correlation coefficient  $R^2$  shows that the adsorption of acid red 3R on HA can be approximated more favorably by the pseudo-second order model ( $R^2=0.994$ ) than the pseudo-first order model ( $R^2=0.9308$ ). The pseudo-second-order model is on the assumption that the adsorption mechanism may be chemical adsorption or chemisorptions, which suggests that the adsorption may involve valence forces through sharing or exchange of electrons between acid red 3R and HA.

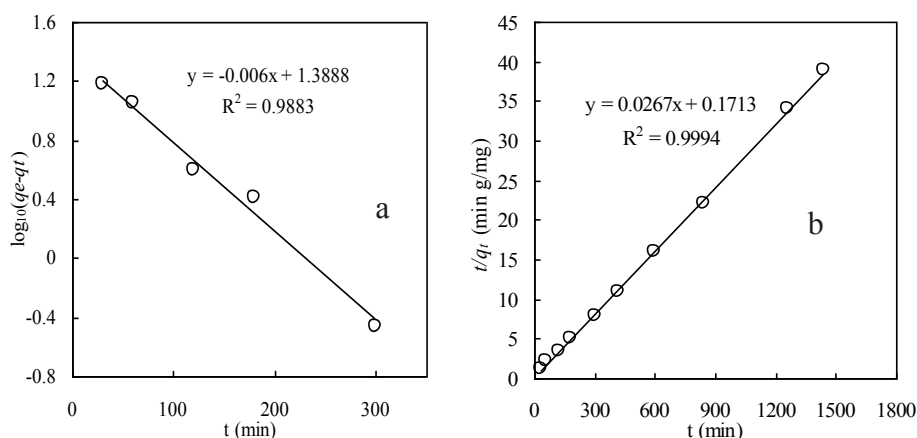


Fig. 3. Lagergren pseudo-first-order (a) and pseudo-second-order (b) kinetics of the dye on flocculent HA.

### 3.3. Adsorption isotherm

Adsorption isotherm model is fundamental in describing the interactive behavior between adsorbate and adsorbent. Analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent, which is one of the main parameters required for the design of an adsorption system. Henry, Freundlich and Langmuir equation are usually used to describe adsorption model. Different models express the mechanism of adsorption. Henry model suggests that the partition of adsorbate between adsorbent and solution is constant, that is partition. The adsorption may take place in the holes of flexible segments of adsorbent. A basic assumption of the Langmuir theory is that the adsorption takes place at specific homogenous sites in the adsorbent. The model does not take into account the variation in adsorption energy. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface [24]. While Freundlich isotherm model is an empirical equation based on the assumption that adsorption occurs on a heterogeneous adsorption surface. It considers multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules [25]. This model can be applied to non-ideal adsorption on heterogeneous surfaces as well as multi-layer adsorption.

Adsorption experiment data of acid red 3R on flocculent HA are shown in Fig. 4. The data were also repressed with Henry, Freundlich and Langmuir equation respectively and the regression coefficients ( $R^2$ ) are 0.959, 0.984 and 0.974 respectively. The result shows that the adsorption of acid red 3R on HA fits Henry, Freundlich and Langmuir models. But the Freundlich model represents the experimental data better on the basis of the values of regression coefficients. This suggests that the adsorption mechanism

may be the electrostatic attraction, to form hydrogen bonds or van der waals' force between molecules of HA and acid red 3R.

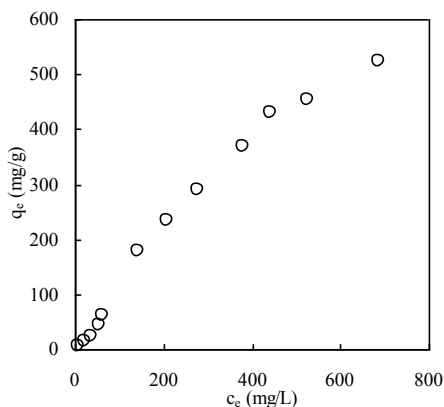


Fig. 4. Isotherm of acid red 3R on flocculent HA.

### 3.4. Effect of the dose of flocculent HA on the sorption

In order to evaluate the effect of flocculent HA dose on dye removal, the experiment with different flocculent HA dosages (from 5 mg to 250 mg) at 30°C was performed. The concentration of the dye in solution was 60 mg/L, pH was 2, and the volume of solution was 50 mL. Fig. 5 shows the amount of dye removal by flocculent HA. The results demonstrate that the removal rate is positively correlated with the amount of HA added. A rapid removal rate increases with the addition of flocculent HA when the dosage is less than 60 mg and then the percentage removal increases slowly. When the amount of HA added is 200 mg, the highest removal is almost reached (98.7%). Such a trend is mainly attributed to the fact that with increase in the amount of the adsorbent, the adsorptive surface area increases which provides a greater number of active sites for adsorption [26].

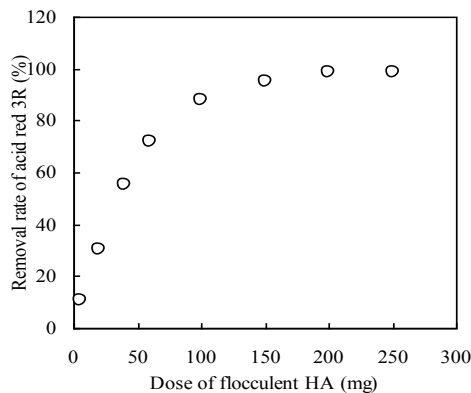


Fig.5. Effect of adsorbent dose on removal of acid red 3R.

### 3.5. Effect of ionic strength on the sorption

There are a number of studies showing the changing of the percentage removal of dye with the

concentration of various electrolyte types in the dye medium [27]. The effect of ionic strength on the removal rate of acid red 3R using flocculent HA was studied at 0.05, 0.1, 0.2, 0.3, 0.5 and 0.5 mol/L NaCl concentrations, 30 °C and pH = 2. The results are demonstrated in Fig. 6. As seen in the figure, the presence of inorganic salt (NaCl) has influenced the removal rate of acid red 3R from aqueous solution. The percentage removal of the dye in aqueous solution decreases with the increase of NaCl concentration, when the concentration of NaCl is less than 0.1 M. Then the value doesn't change with the increase of the inorganic salt. The results suggest that the presence of inorganic salt (NaCl) will hinder the adsorption of the dye on flocculent HA. Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions were attractive, an increase in ionic strength will decrease the adsorption capacity. Conversely, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption [28-29]. The results suggest the electrostatic forces between flocculent HA surface and acid red 3R ions were attractive.

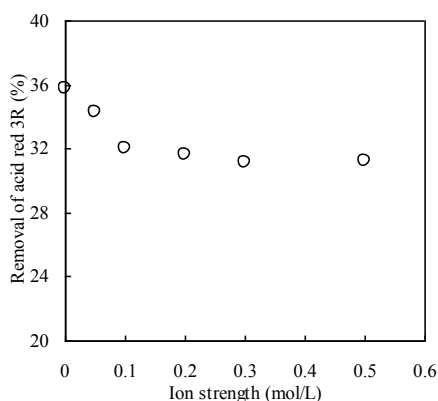


Fig. 6. Effect of ionic strength on removal of acid red 3R.

#### 4 Conclusions

From what discussed above, conclusions can be made as follows:

(1) Adsorption of acid red 3R on flocculent HA can reach equilibrium quickly (180 min) because of the high specific surface of flocculent HA. The adsorption kinetics obeys the pseudo-second order model ( $R^2=0.994$ ), which suggests that the adsorption may involve valence forces through sharing or exchange of electrons between acid red 3R and flocculent HA.

(2) The adsorption of acid red 3R on flocculent HA can be described by Freundlich equation on the basis of the value of regression coefficient ( $R^2=0.984$ ). This suggests that the adsorption mechanism may be the electrostatic attraction, to form hydrogen bonds or van der waals' force between molecules of HA and acid red 3R.

(3) The removal rate of the dye increases with the increase of the flocculent HA dose, while the value decreases with the addition of NaCl.

(4) Flocculent HA isolated from lignite can be used an adsorbent to remove dyes from aqueous solution.

#### References

- [1] Robinson T, Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Res* 2002, **36**: 2824-2830.
- [2] Lee JW, Choi SP, Thiruvengatachari R, Shim WG, Moon H. Evaluation of the performance of adsorption and coagulation



- processes for the maximum removal of reactive dyes. *Dyes Pigm* 2006, **69**: 196-203.
- [3] Al-Degs Y, Khraisheh AM, Allen SJ, Ahmad MN. Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. *Water Res* 2000, **34**: 927-935.
- [4] Chen KC, Wu JY, Huang CC, Liang YM, Hwang SCJ. Decolorization of azo dye using PVA-immobilized microorganisms. *J Biotechnol* 2003, **101**: 241-252.
- [5] Jain AK, Gupta VK, Bhatnagar A. Utilization of industrial waste products as adsorbents for the removal of dyes. *J Hazard Mater* 2003, **101**: 31-42.
- [6] Ho YS, McKay G. Sorption of dyes and copper ions onto biosorbents. *Process Biochem* 2003, **38**: 1047-1061.
- [7] Derbyshire F, Jagtoyen M, Andrews R, Rao A, Martin-Gullon I, Gruke E. Carbon materials in environmental applications, in: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*, vol. 27, Marcel Dekker, New York, 2001, p.60-66
- [8] McKay G. The adsorption of dyestuffs from aqueous solution using activated carbon: analytical solution for batch adsorption based on external mass transfer and pore diffusion. *Chem Eng J* 1983, **27**: 187-196.
- [9] Ramakrishna KR, Viraraghavan T. Dye removal using low cost adsorbents. *Water Sci Technol* 1997, **36**: 189-196.
- [10] Juang RS, Tseng RL, Wu FC. Adsorption behavior of reactive dyes from aqueous solutions on chitosan. *J Chem Technol Biotechnol* 1997, **70**: 391-399.
- [11] McKay G. Analytical solution using a pore diffusion model for a pseudo-irreversible isotherm for the adsorption of basic dye on silica. *AIChE J* 1984, **30**: 692-697.
- [12] Hu TL. Removal of reactive dyes from aqueous solution by different bacterial genera. *Water Sci Technol* 1996, **34**: 89-95.
- [13] Namasivayam C, Prabha D, Kumutha M. Removal of direct red and acid brilliant blue by adsorption on to banana pith. *Biores Technol* 1998, **64**: 77-79.
- [14] Aksu Z. Biosorption of reactive dyes by dried activated sludge: equilibrium and kinetic modelling. *Biochem Eng J* 2001, **7**: 79-84.
- [15] Vandevivere PC, Bianchi R, Verstrate W. Treatment and reuse of waste-water from the textile wetprocessing industry. *J Chem Technol Biotechnol* 1998, **72**: 289-302.
- [16] Stevenson FJ. *Humus Chemistry: Genesis, Composition, Reactions*. New York: John Wiley & Sons, 1994, p. 34-35
- [17] Kopinke FD, Georgi A, Mackenzie K. Sorption of Pyrene to Dissolved Humic Substances and Related Model Polymers. 1. Structure-Property Correlation. *Environ Sci Technol* 2001, **35**: 2536-2542.
- [18] Matsuda M, Kaminaga A, Hayakawa K, Fan MH. Surfactant binding by humic acids in the presence of divalent metal salts. *Colloids Surf A: Physicochem Eng Aspects* 2009, **347**: 45-49.
- [19] Kuwatsuka S, Watanabe A, Itoh K, Arai S. Comparison of two methods of preparation of humic acids and fulvic acids, IHSS method and NAGOYA method. *Soil Sci Plant Nutr* 1992, **38**: 23-30.
- [20] Ho YS, McKay G. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *Can J Chem Eng* 1998, **76**: 822-827.
- [21] Periasamy K, Namasvayam C. Process Development for Removal and Recovery of Cadmium from Wastewater by a Low-Cost Adsorbent: Adsorption Rates and Equilibrium Studies. *Ind Eng Chem Res* 1994, **33**: 317-320.
- [22] Saeed A, Iqbal M, Zafar SI. Immobilization of *Trichoderma viride* for enhanced methylene blue biosorption: Batch and column studies. *J Hazard Mater* 2009, **168**: 406-415.
- [23] Wu FC, Tseng RL, Huang SC, Juang RS. Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review. *Chem Eng J* 2009, **151**: 1-9.
- [24] Afkhami A, Moosavi R. Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles. *J Hazard Mater* 2010, **174**: 398-403.
- [25] Chatterjee S, Lee DS, Lee MW, Woo SH. Enhanced adsorption of congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyltrimethyl ammonium bromide. *Bioresour Technol* 2009, **100**: 2803-2809.
- [26] Hem L, Garg VK, Gupta RK. Removal of a basic dye from aqueous solution by adsorption using *Parthenium hysterophorus*: An agricultural waste. *Dyes Pigm* 2007, **74**: 653-658.
- [27] Alkan M, Dogan M, Turhan Y, Demirbas O, Turan P. Adsorption kinetics and mechanism of maxilon blue 5G dye on sepiolite from aqueous solutions. *Chem Eng J* 2008, **139**: 213-223.
- [28] Newcombe G, Drikas M. Adsorption of NOM activated carbon: electrostatic and non-electrostatic effects. *Carbon* 1997, **35**: 1239-1250.
- [29] Alberghina G, Bianchini R, Fichera M, Fisichella S. Dimerization of Cibacron Blue F3GA and other dyes: influence of salts and temperature. *Dyes Pigm* 2000, **46**: 129-137.