Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.950996

56 (2015) 1520–1525
November

Taylor & Francis
Taylor & Francis Group

Removal of dark blue-GL from wastewater using water hyacinth: a study of equilibrium adsorption isotherm

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Received 19 February 2014; Accepted 12 July 2014

ABSTRACT

The present investigation demonstrates that water hyacinth root is a potential adsorbent for the removal of dark blue-GL dye from wastewater by batch process. Various operating parameters such as the adsorption capacity, initial dye concentration, contact time, effect of pH, and adsorbent dosage were examined at different experimental conditions. The effect of pH and dye concentration found to be crucial, have been optimized, and the maximum recovery (~90%) was detected at pH 3 and concentration 150 ppm. The separation of dark blue-GL is proportionally related to the adsorbent dosage, and up to 77% dye was recovered for the dose 1.5 g/L. Langmuir adsorption isotherm model of the adsorption process was carried out at the equilibrium concentration of dark blue-GL uptake, and the corresponding data were analyzed by the least square methods. Kinetic parameters calculated from the tentative data could be fitted well to a pseudo-second-order kinetic model. These results point out aptness of the adsorbent in the niche area due to high adsorption capacity (~24 g/kg) and can be applied in the execution of dark blue-GL-enriched wastewater.

Keywords: Water hyacinth; Adsorption; Dark blue-GL; Kinetics; Wastewater

1. Introduction

Dyes are extensively used in various fields of advanced technology, e.g. in diverse kindling of the textile industries [1]. Many industries like plastics, paper, textile, and cosmetics use dyes to color their products. About 634,900 metric tons of dyes are produced worldwide each year, and approximately 10–15% of them are discharged as effluent [2]. These dyes are common water pollutants, and they may be frequently detected in trace quantities in industrial wastewater. The discharge of colored wastewater from industries into natural streams has caused many significant problems, such as increasing the toxicity of the effluent and also reducing the light penetration, which has a derogatory effect on photosynthetic phenomenon. In addition, some dyes are either toxic or mutagenic and carcinogenic in nature [3–5]. Their presence in water, even at very low concentrations, is highly visible and undesirable. In addition, many dyes are difficult to degrade due to their complex aromatic

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structure, and they tend to persist in the environment creating serious water quality and public health problems. Therefore, it would be advantageous to develop technologies to eliminate them. A number of conventional biological treatment processes are not very effective for treating wastewater owing to low biodegradability of dyes [6]. There are various methods for dye removals, which include coagulation and chemical oxidation, membrane separation, reverse osmosis, and aerobic as well as anaerobic microbial degradation, but all of these methods suffer from critical drawbacks and none of them are doing well for completely removing the color from wastewater [7]. Dyes can be effectively removed by adsorption process in which dissolved dye compounds were attached to the surface of adsorbents with weak Vander Walls' forces.

Apart from the commercially available synthetic adsorbents, researchers have invented many low-cost and biodegradable effective adsorbents, which are used for the removal of different dyes from aqueous solutions at different operating conditions. Some of the adsorbent materials that have been successfully employed for the removal of dye stuffs from aqueous solutions include but not limited to activated carbon [8], peat [9], chitin [10], silica [11], hardwood [12], hardwood sawdust [13], bagasse pith [14], fly ash [15, 16], mixture of fly ash and coal [17], chitosan fiber [18], paddy straw [19], rice husk [20], slag [21], chitosan [22], acid-treated spent bleaching earth [23], palm fruit bunch [24], and bone char [25]. The dark blue-GL has wider applications, which include dyeing cotton and viscose fabric, silk and nylon fabric, wools, etc. in textile industries. Acute exposure to the dark blue-GL causes health hazards like increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [26]. Recently, there is a growing interest in using low-cost and non conventional alternative adsorbent instead of traditional one. Khan et al. [27] lately studied adsorption and desorption characteristics of water hyacinth root (WHR) powder for the removal of Indosol dark blue-GL in batch mode. This is an extended investigation of our previous work regarding utilization of WHR as an adsorbent for the removal of the dark blue-GL from its aqueous solution, optimization of sorption parameters, and study of Langmuir isotherm and pseudo-second-order kinetic model.

2. Materials and methods

2.1. Preparation of adsorbent

Water hyacinth is a free-floating perennial aquatic plant available in Bangladesh. Roots of water hyacinth were collected from ponds of Sylhet, Bangladesh. Those were thoroughly washed with water for several times, which was followed by boiling in water for 30 min. Then WHR was soaked in 0.1 M HCl for 20 min followed by washing with distilled water. The roots were then dried in an oven at the temperature range of 90–100˚C for 8 h. The dried roots were milled into powder and used for the entire experiment as an adsorbent.

2.2. Preparation of adsorbate

Dark blue-GL was used as an adsorbate. Stock solution of dark blue-GL (MW 782.17 g) was prepared in double distilled water. For the determination of adsorption of dye, the solution of various concentrations, e.g. 50, 100, and 150 ppm was prepared. The pH of the solutions was analyzed over the pH range from 2 to 7. The absorbance of solutions was measured by a spectrophotometer of wave length 587 nm where maximum absorbance was observed at a temperature 26 ± 2˚C and pH 3.

2.3. Adsorbent dosage

The effect of powdered water hyacinth dosage on the amount of adsorption of dark blue-GL solution was obtained by mixing 100 ml of dark blue-GL solution of initial concentrations of 50, 100, and 150 ppm with different amounts (0.25, 0.5, 0.75, 1.0, 1.5, 1.75, and 2.0 g) of powdered water hyacinth in stopper conical flasks. Each sample was then shaken for 7 h at a constant oscillation of 500 osc/min. The samples were then centrifuged, and the concentrations in the supernatant solutions were then analyzed as before.

2.4. Equilibrium adsorption isotherm

Equilibrium studies were carried out by batch technique. In this study, a series of 250 ml stopper conical flasks containing 1.0 g of powdered water hyacinth with 100 ml of dark blue-GL solution of different initial concentrations of 50, 100, and 150 ppm were taken. The samples were then shaken at a constant oscillation of 500 osc/min for 7 h. After the attainment of equilibrium, the samples of various concentrations were analyzed. Each experiment was repeated under identical conditions, and the average values were taken. The amount of adsorption at equilibrium, q_e (kg/kg), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (kg/m^3) are the liquid-phase concentrations of dye at initial and at equilibrium, respectively. V is the volume of the solution (m^3), and W is the mass of dry adsorbent used (kg).

2.5. Adsorption kinetics

For sorption kinetic study, batch technique was selected for its simplicity. Here, the experiment was carried out by contacting 200 ml dark blue-GL solution of different initial concentrations ranging from 50 to 150 ppm with 1 g of powdered water hyacinth in 250 ml stopper conical flask. The samples were then shaken at a constant oscillation speed of 500 osc/min for 7 h. Samples were then pipetted out at different time intervals. The collected samples were then centrifuged, and the concentration in the supernatant solution was analyzed. The amount of adsorption was calculated according to the Eq. (1) considering q_e as q_t and C_e as C_t at time t.

To investigate the mechanism of sorption, the constants of adsorption were determined by using a pseudo-second-order mechanism. The adsorption kinetics may be described by the pseudo-second-order model [28] that is shown in Eq. (2).

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{2}$$

where $k_2$is the rate constant of pseudo-second-order sorption (kg/(kg min). The integrated form of the above equation becomes as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

The amount of adsorption (q_e) and the rate constant (k) can be determined from the plot of t/q against t.

3. Result and discussion

3.1. Effect of pH

The effect of pH on dye adsorption has been reported from 2 to 7 in Fig. 1. As seen from the figure, the maximum dye adsorption (~90%) was observed at pH 3.0 and a gradual decrease in adsorption takes place with the increase in pH. Only 20% dye adsorption took place at pH 7. The higher adsorption at lower pH can be attributed to the electrostatic attraction between charged dye molecules and charged cell surface [29].

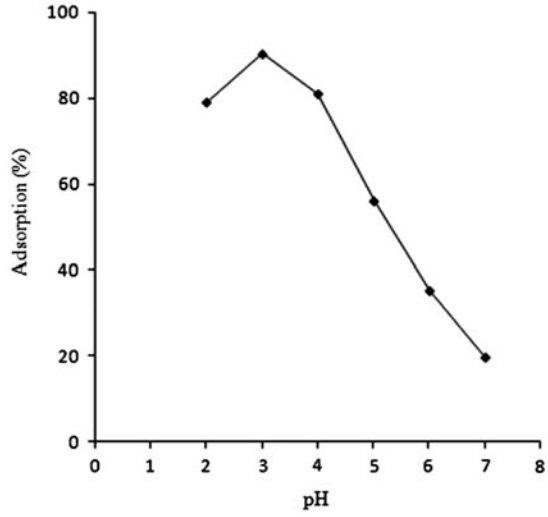

Fig. 1. Effect of pH for the removal of dark blue-GL by water hyacinth: concentration 150 ppm, time 7 h, and speed 500 osc/min.

3.2. Effect of adsorbent doses

The effect of dark blue-GL removal at pH 3 with varying amount of adsorbent dosages is depicted in Fig. 2. The separation of dark blue-GL is somehow proportional to adsorbent doses. It was found that the concentration of dye had very little effect on dye removal at any particular adsorbent dose. However, sample of 150 ppm shows best results. When adsorbent dose was 0.25 g/L, the removal turned into ~22%, and it

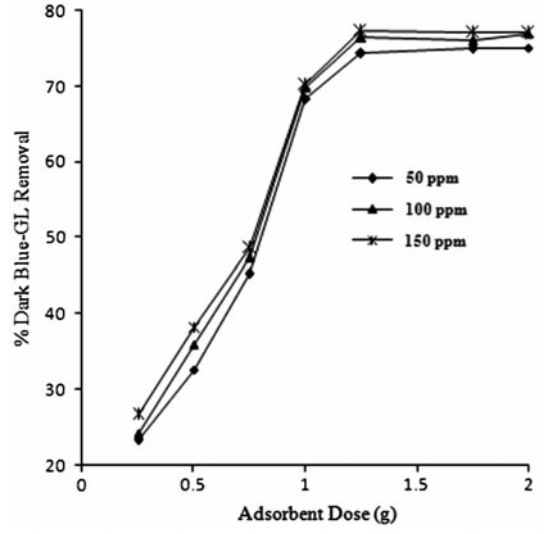

Fig. 2. Effect of amount of adsorbent for the removal of dark blue-GL of various concentrations using water hyacinth at pH 3.

increased almost linearly up to ~45% at dose 1 g/L. The effect of adsorbent doses from 1 to 1.25 g/L is the most momentous, and in this region, from 45 to 70% dark blue-GL was found to be removed. With further increase in doses (1.25–1.5 g/L), separation of dye increases (70–77%), which eventually becomes constant. The increase in the amount of dye removal with adsorbent doses is due to greater availability of adsorbent surface area [30] and hence more active sites.

3.3. Adsorption isotherm

Figs. 3 and 4 show Langmuir adsorption isotherm plots regarding the effect of equilibrium concentration of WHR on dark blue-GL uptake. The performance of adsorbents is usually determined by their uptake capacity. Adsorbents can be compared based on their respective maximum uptake values, q_0, which can be calculated by fitting the Langmuir isotherm model to the actual experimental data if it fits. This approach is feasible if q_0 reaches a plateau. A high affinity between the adsorbent and adsorbate reflected in good uptake values at low concentrations, C_e, is desirable. This is characterized by a steep rise of the isotherm curve close to its origin. An adsorbent better at low concentrations may be inferior at higher ones, and vice versa. Therefore, it is necessary to compare the adsorbent capacity at low C_e and also at high C_e for the same pH of the solution.

The isotherm data were calculated from the least squares method, and the values of the parameters of the Langmuir model from Figs. 3 and 4 and the related correlation coefficients (R^2) are listed in Table 1. The parameter indicates that pH can enhance the dye removal effectively. The maximum sorption capacity of powdered WHR was found to be 60.2 mg DB dye/g at pH 3, while that at pH 5 was only 33.1 mg DB dye/g. This result is a verification of our previous investigation as shown in Fig. 1, i.e. the maximum adsorption was detected at pH 3. In addition, the Langmuir equation nicely simulates the sorption equilibrium data.

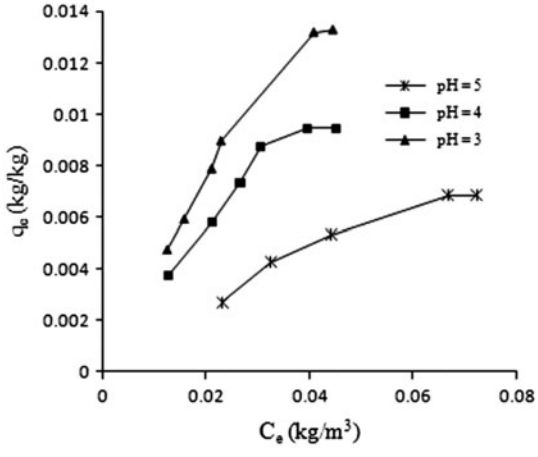

Fig. 3. Langmuir adsorption isotherm of dark blue-GL removal using powdered WHR at different pH. Condition: concentration 150 ppm, time 7 h, and speed 500 osc/min.

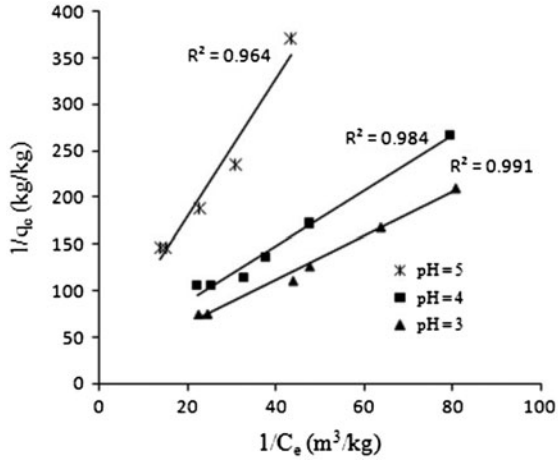

Fig. 4. Linear fitting of Langmuir adsorption isotherm of dark blue-GL removal using powdered WHR at different pH. Condition: concentration 150 ppm, time 7 h, and speed 500 osc/min.

In general, a good adsorbent being one with a high q_0, a steep initial adsorption isotherm slope, and low Langmuir constants signifies a strong affinity between water hyacinth and dark blue-GL (Figs. 3 and 4). The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, K_R, which is used to predict whether an adsorption system is favorable or unfavorable. The separation factor is defined by the following relationship:

$$K_R = \frac{1}{1 + K_L C_0} \tag{4}$$

Table 1
Langmuir parameters of dark blue-GL at concentration C_0 = 150 ppm adsorbed by powdered WHR

Sample pH	q_0 (kg/kg)	K_L(L/mg)	R^2
3	0.0602	7.03	0.99
4	0.0345	9.76	0.98
5	0.0331	4.07	0.96

where K_R is a dimensionless separation factor, C_0 is initial dye concentration (mg/dm^3), and K_L is the Langmuir constant (dm^3/mg). The parameter K_R indicates the shape of the isotherm accordingly: $K_R > 1$ (unfavorable), $K_R = 1$ (linear), $0 < K_R < 1$ (favorable), and $K_R = 0$ (irreversible).

The values of K_R for initial dye concentrations from 50 to 150 ppm were found to be from 683×10^{-6} to 489×10^{-5}. The K_R values indicate that adsorption of dark blue-GL onto powdered WHR is favorable.

3.4. Effect of contact time and initial dye concentration

The effect of contact time on dark blue-GL adsorption by powdered WHR at different initial concentrations ranging from 50 to 150 ppm is shown in Fig. 5. It is evident that the extent of adsorption is rapid for the first 50 min, then proceeded at a slower rate, and finally attained equilibrium, where dye concentration did not vary significantly after 110 min from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 110 min. It is basically due to saturation of the active site which does not allow further adsorption to take place. As the initial concentration of dye increased from 50 to 150 ppm, the amount of dark blue-GL dye adsorbed onto powdered WHR increased from 3.9 to 24.1 g/kg at pH 3 (Fig. 5). This indicated that the initial concentration and pH strongly affect adsorption capacity.

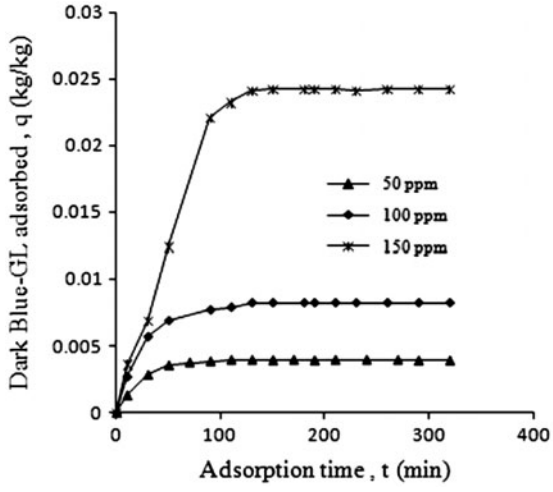

Fig. 5. Effect of contact time for the removal of dark blue-GL of various concentrations using water hyacinth at pH 3 and speed 500 osc/min.

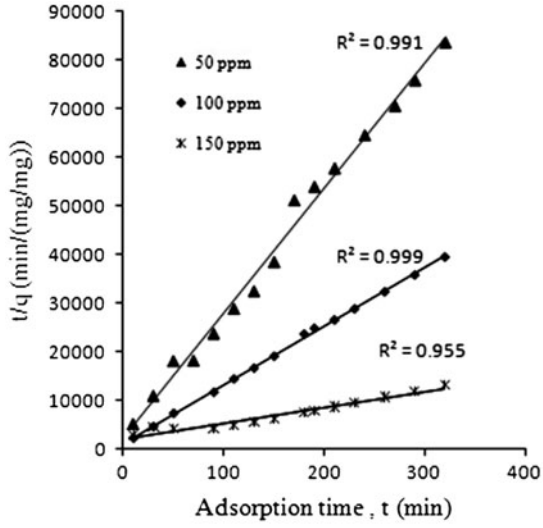

Fig. 6. Pseudo-second-order kinetics for the removal of dark blue-GL of various concentrations using powdered WHR at pH 3 and speed 500 osc/min.

3.5. Adsorption kinetics

Several mechanisms can be used to express the mechanism of solute adsorption onto an adsorbent. For the adsorption purpose, in general, a pseudo-second-order kinetic model is used to understand and express the sorption mechanism. In this study too, a pseudo-second-order kinetic model was used to determine various essential parameters.

Dark blue-GL dye adsorption kinetics was described well by common kinetic models (Fig. 6 and Table 2). The pseudo-second-order model with respect to dye adsorption fits our data well, yielding R2 values for initial dye concentrations of 50, 100, and 150 ppm. Corresponding rate constants for these initial values were 27.72, 13.31, and 0.57 kg/(kg min). A pseudo-first-order model with respect to dark blue-GL dye adsorption advocated by [28] was also analyzed by our group, and it was found that the results did not match well (data not inserted due to simplicity). Hence, the pseudo-second-order model better represented the adsorption kinetics. Similar phenomenon has been observed in the

Table 2
Pseudo-second-order parameters for dark blue-GL that adsorbed onto water hyacinth at pH 3

Pseudo-second-order kinetic model		
k_2 (kg/(kg min))	q_e (kg/kg)	R^2
27.72	0.003894	0.991
13.31	0.008278	0.999
0.57	0.030349	0.955

removal of methylene blue dye by sawdust and bamboo-based activated carbon adsorbents.

4. Conclusion

WHR is an effective adsorbent for the removal of dark blue-GL dye from the industrial wastewater. pH and dye concentration have been optimized for the maximum recovery, and the effect of the adsorbent doses as well evaluated. Kinetic study of the adsorption process has been carried out, and at the optimum conditions (pH 3 and dye concentration 150 ppm), the system is comparatively fast. The effect of equilibrium concentration on dark blue-GL removal has been simulated by Langmuir adsorption isotherm. Pseudo-second-order kinetics for the removal of dark blue-GL has been described reasonably by common kinetic model.

References

[1] S.S. Azhar, A.G. Liew, D. Suhardy, K.F. Hafiz, M.D.I. Hatim, Dye removal from aqueous solution by using adsorption on treated sugarcane bagasse, Am. J. Appl. Sci. 2 (2005) 1499–1503.
[2] R. Gong, M. Li, C. Yang, Y. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, J. Hazard. Mater. 121 (2005) 247–250.
[3] F. Derbyshire, X. Jagtoyen, M. Andrews, R. Rao, A.I. MartinGullon, E. Grulke, Carbon materials in environmental applications, in: L.R. Radovic (Ed.), Marcel Dekker, Chemistry and Physics of Carbon, New York, NY, 2003, pp. 1–66.
[4] G. McKay, J.F. Porter, G.R. Prasad, The removal of dye colours from aqueous solutions by adsorption on low-cost materials, Water Air Soil Pollut. 114 (1998) 423–438.
[5] A.K. Jain, V.K. Gupta, A. Bhatnagar, Suhas, Utilization of industrial waste products as adsorbents for the removal of dyes, J. Hazard. Mater. 101 (2003) 31–42.
[6] S. Seshadri, P.L. Bishop, A.M. Agha, Anaerobic/aerobic treatment of selected azo dyes in wastewater, Waste Manage. 14 (1994) 127–137.
[7] M.T. Sulak, E. Demirbas, M. Kobya, Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran, J. Bioresour. Technol. 98 (2007) 2590–2598.
[8] R.L. Dedrick, R.B. Beckmann, Kinetics of adsorption by activated carbon from dilute aqueous solution, AIChE J. 3 (1967) 68–75.
[9] G. McKay, S.J. Allen, I.F. McConvey, M.S. Otterburn, Transport processes in the sorption of colored ions by peat particles, J. Colloid Inter. Sci. 80 (1981) 323–339.
[10] G. McKay, H.S. Blair, J.S. Gardner, Rate studies for the adsorption of dyestuffs on chitin, J. Colloid Inter. Sci. 95 (1983) 108–119.
[11] G. McKay, Analytical solution using a pore diffusion model for a pseudoirreversible isotherm for the adsorption of basic dye on silica, AIChE J. 30 (1984) 692–697.
[12] H.M. Asfour, O.A. Fadeli, M.M. Nasser, M.S. El-Geundi, Equilibrium studies on adsorption of basic dyes on hardwood, J. Chem. Technol. Biotechnol. 35 (1985) 21–27.
[13] H.M. Asfour, O.A. Fadeli, M.M. Nasser, M.S. El-Geundi, Colour removal from textile effluents using hardwood sawdust as adsorbent, J. Chem. Technol. Biotechnol. 35 (1985) 28–35.
[14] G. McKay, M. El Geundi, M.M. Nassar, Equilibrium studies during the removal of dyestuff's from aqueous solutions using bagasse pitch, Water Res. 21 (1987) 1513–1520.
[15] S.K. Khare, K. Panday, R.M. Srivastava, V.N. Singh, Removal of Victoria Blue from aqueous solutions by fly ash, J. Chem. Technol. Biotechnol. 38 (1987) 99–104.
[16] G.S. Gupta, G. Prasad, V.H. Singh, Removal of chrome dye from aqueous solutions by fly ash, Water Air Soil Pollut. 37 (1988) 13–24.
[17] G.S. Gupta, G. Prasad, V.H. Singh, Removal of chrome dye from aqueous solutions by mixed adsorbents: Fly ash and coal, Water Res. 24 (1990) 45–50.
[18] H. Yoshida, S. Fukuda, S. Okamota, T. Kataoka, Recovery of direct dye and acid dye by adsorption on chitosan fiber equilibrium, Water Sci. Technol. 23 (1991) 1667–1676.
[19] D. Narmata, A. Manzoor, Dye adsorption by a new low cost material Congo red, Ind. J. Environ. Protec. 13 (1993) 570–576.
[20] C.K. Lee, K.S. Low, Quaternized rice husk as sorbent for reactive dyes, Bioresour. Technol. 61 (1997) 121–125.
[21] K.R. Ramakrishna, T. Viraraghavan, Use of slag for dye removal, Waste Manage. 17 (1997) 483–488.
[22] R.S. Juang, R.K.L. Tseng, F.C. Wu, S.H. Lee, Adsorption behaviour of reactive dyes from aqueous solution on chitosan, J. Chem. Technol. Biotechnol. 70 (1997) 391–399.
[23] C.K. Lee, K.S. Low, Removal of some organic dyes by acid-treated spent bleaching earth, Process Biochem. 34 (1999) 451–465.
[24] M.M. Nassar, Intraparticle diffusion of basic red and basic yellow dyes on palm fruit bunch, Water Sci. Technol. 40 (1999) 133–139.
[25] D.C.K. Ko, J.F. Porter, G. McKay, Optimised correlations for the fixed-bed adsorption of metal ions on bone char, Chem. Eng. Sci. 55 (2000) 5819–5829.
[26] R. Ahmad, R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, J. Environ. Manage. 91 (2010) 1032–1038.
[27] M.M.R. Khan, M.Z.B. Mukhlish, M.S.I. Mazumder, K. Ferdous, D.M.R. Prasad, Z. Hassan, Uptake of Indosol Dark-blue GL dye from aqueous solution by water hyacinth roots powder: Adsorption and desorption study, Int. J. Environ. Sci. Technol. 11 (2014) 1027–1034.
[28] Y.S. Ho, G. Mckay, Pseudo-second-order model for sorption process, Process Biochem. 34 (1999) 451–465.
[29] E. Zeynep, N.A. Filiz, Adsorption of Reactive Black 5 from an aqueous solution: Equilibrium and kinetic studies, Desalination 194 (2006) 1–10.
[30] N.M. Agyei, C.A. Strydom, J.H. Potgieter, An investigation of phosphate ion adsorption from aqueous solution by fly ash and slag, Cem. Concr. Res. 30 (2000) 823–826.