

Sorption of Chromium (VI) by Spent Grain Under Batch Conditions

KUN-SHE LOW, CHNOONG KHENG LEE, CHOY HOONG LOW

Chemistry Department, Faculty of Science and Environmental Studies, Universiti Putra Malaysia, UPM 43400, Serdang, Selangor, Malaysia

Received 5 June 2000; accepted 22 February 2001

ABSTRACT: Batch experiments were performed to evaluate the ability of spent grain to remove chromium (VI) from aqueous solution. Parameters investigated include pH, contact time, sorbent dosage, agitation rate, and the presence of other anions. Application of the Langmuir isotherm to the Cr(VI)–spent grain system provided a maximum sorption capacity of 18.94 mg/g. This value compares favorably with other reported values for low-cost materials. Anions such as phosphate, arsenate, nitrate, and sulfate were antagonistic toward the uptake of Cr(VI) by spent grain. It was successful in removing Cr(VI) from a sample of electroplating waste. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2128–2134, 2001

Key words: low-cost material; spent grain; sorption; chromium

INTRODUCTION

Chromium is an essential nutrient for plant and animal metabolism. However, the increasing accumulation of chromium in the environment from industrial outputs has caused great concern. Chromium-contaminated wastewaters can originate from dye and pigment manufacturing, wood preserving, electroplating, and leather tanning. Chromium exists in either the +3 or +6 oxidation state, given that all other oxidation states are not stable in aqueous systems. Chromium(VI) is 100 to 1000 times more toxic to an organism than Cr(III).

Conventional methods of its removal are chemical reduction [from Cr(VI) to Cr(III)], electrochemical treatment, and adsorption process. Such methods can be expensive. An alternative method

that uses low-cost materials was recently reported. A low-cost sorbent is defined as one that is abundant in nature or is a by-product or waste material from another industry.¹ Low-cost materials investigated for their sorptive potential for Cr(VI) include various nonliving biomasses of microorganisms,² seaweed,³ modified rice hull,⁴ and peat.⁵ In our continued effort to exploit low-cost materials for the removal of organic and inorganic pollutants in an aqueous environment we investigated the potential of spent grain, a brewery waste product, as a sorbent for the removal of Cr(VI). Factors such as pH, initial concentration, temperature, dosage, and the presence of other anions that generally affect the sorption process were investigated.

EXPERIMENTAL

Materials

Fresh spent grain was obtained from a local brewery located in Selangor. The grain was washed

Correspondence to: Kun-She Low.
Contract grant sponsor: MPKSN; contract grant number: IRPA 09-0204-0061.

Journal of Applied Polymer Science, Vol. 82, 2128–2134 (2001)
© 2001 John Wiley & Sons, Inc.

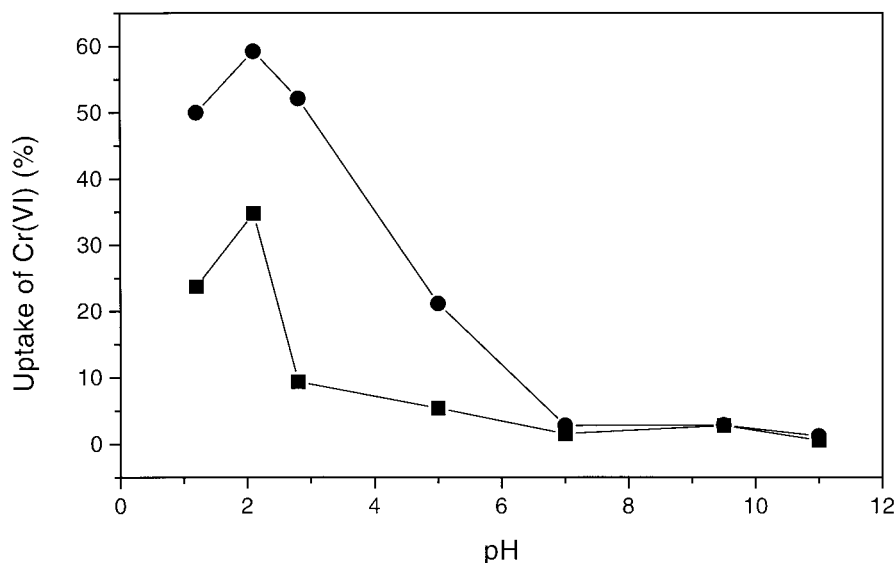


Figure 1 Effect of pH on the uptake of Cr(VI) by spent grain: acid-treated spent grain (●); untreated spent grain (■).

thoroughly with distilled water. It was dried at 60°C and ground to pass through a 1-mm sieve. Preliminary studies using spent grain treated with acid and base were carried out to optimize the sorption of the Cr(VI) ion. Maximum sorption was obtained by treating the grain with 1M HCl solution at room temperature for 1 h in a weight ratio of 1 : 10. Excess of acid was removed with water and the acidified material was dried at room temperature.

Methods

The effect of pH on Cr(VI) uptake was carried out with 0.1 g of spent grain in 20 mL of Cr(VI) solution. The pH of the solution was adjusted with 0.1M HCl or NaOH solution. The mixture was agitated on a gyratory shaker at 150 rpm at room temperature ($29 \pm 2^\circ\text{C}$). At the end of the experiment the sample was centrifuged at 3500 rpm for 5 min and the supernatant was analyzed for its metal ions using an inductively coupled plasma-atomic emission spectrometer (Perkin-Elmer 1000; Perkin Elmer Cetus Instruments, Norwalk, CT). Controls were also performed with spent grain to ensure that Cr(VI) uptake did not occur via metal precipitation or sorption on the vessel wall. All experiments were performed in duplicate and the averages of the results taken.

Because the optimum sorption occurred at pH 2 all subsequent experiments were conducted at this pH unless otherwise stated.

Anions that might affect the sorption process were investigated. They were SO_4^{2-} , NO_3^- , Cl^- , and PO_4^{3-} .

The effect of temperature was studied by shaking the Cr(VI)-spent grain mixture in a thermostatically controlled water bath until equilibrium was established.

RESULTS AND DISCUSSION

Effect of Chemical Treatment on Sorption

At pH 2 [optimum sorption of Cr(VI)] the uptake of Cr(VI) by untreated, base-treated, and acid-treated spent grains under similar conditions were 48.8, 31.4, and 73.5%, respectively. Higher uptake of acid-washed spent grain was probably caused by protonation of spent grain during acid treatment.

Effect of pH

The uptake of Cr(VI) as a function of pH is shown in Figure 1. The uptake increased with decreasing pH value. The maximum uptake occurred at pH 2 (59%) and thereafter decreased when the pH of the solution became very acidic (<2). A similar uptake pattern, whereby decreasing the pH from neutral to acidic initially increased the Cr(VI) uptake but further decreased in pH (below pH 2) caused the uptake to decrease, was reported by Sharma and For-

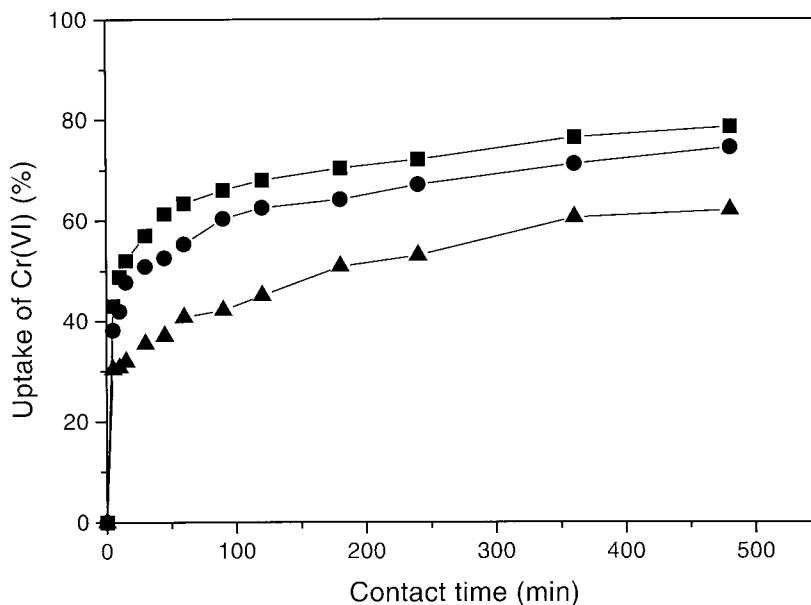


Figure 2 Uptake of Cr(VI) as a function of initial concentration of Cr(VI) solution: 25 mg/L (■); 50 mg/L (●), and 100 mg/L (▲).

ster⁶ in their study on the sorption of Cr(VI) by various kinds of biomass. Kratochvil et al.³ observed a similar trend in the study of uptake of seaweed as a function of pH. A mechanism for the uptake of Cr(VI) as a function of pH was proposed. The uptake of Cr(VI) by seaweed includes two processes: (1) sorption, most likely by anion exchange; and (2) reduction of Cr(VI) to Cr(III) at a pH lower than the optimum. The optimum pH for Cr(VI) uptake lies in the region where the two processes overlap. A similar mechanism could be operating in Cr(VI)-spent grain system and experimental results show the optimum pH to be in the vicinity of pH 2.

Effect of Contact Time and Initial Concentration

The rates of sorption of Cr(VI) at different initial concentrations are shown in Figure 2. The initial rate was rapid and thereafter sorption was gradual and pseudo-equilibrium was reached after 480 min. At pseudo-equilibrium, the amounts of Cr(VI) sorbed at 25, 50, and 100 mg/L Cr(VI) were 3.93 (78.6%), 7.45 (74.5%), and 12.42 (62.3%) mg/g of Cr(VI), respectively. It is evident that the amount sorbed on the solid phase increased with increasing concentration of the solution. However, the percentage removal of Cr(VI) increased with decreasing concentration.

Various models have been used to describe the kinetics of sorption. The first-order kinetic pro-

cess derived by Lagergren⁷ has been widely used. However, the second-order equation to describe sorption has recently been applied by various researchers.⁸⁻¹⁰ Application of the present sorption data to Lagergren was not successful. Its conformity to the second-order rate equation of the expression $t/q_t = (1/k) + (t/q_e)$ is shown in Figure 3, where t is the contact time (min), q_t and q_e are the amounts sorbed at time t and at equilibrium (mg/g), and k is the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The amounts sorbed at equilibrium were 3.95, 7.47, and 12.66 mg/g for 25, 50, 100 mg/g Cr(VI) solutions, respectively. These values compare favorably with experimental values of 3.93, 7.45, and 12.45 mg/g, respectively. The rate constants for 25, 50, and 100 mg/g Cr(VI) solution are 2.06×10^{-2} , 7.92×10^{-3} , and 2.91×10^{-3} g/mg, respectively, showing a decreasing value as concentration increases.

Effect of Agitation Rate

The effect of agitation rate on the uptake of Cr(VI) is shown in Figure 4. When the rate was increased from 100 to 150 rpm, the uptake increased from 69.3 to 74.5%. This is ascribed to the reduction of the film boundary layer surrounding the spent grain particles. The external mass transfer was no longer important when the system was well agitated (>150 rpm). A similar behavior was reported by Low et al.¹⁰ in the study

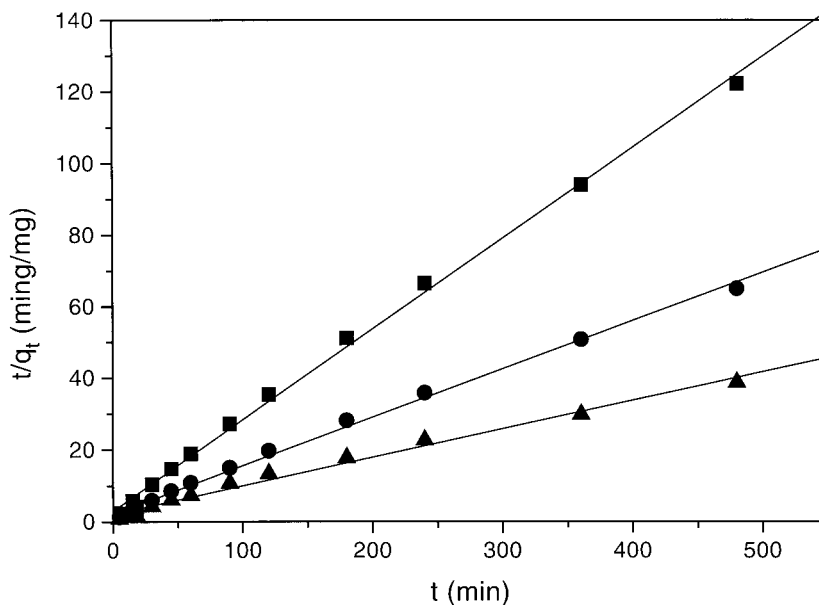


Figure 3 Plots of sorption t/q_t versus time t for different initial concentrations of Cr(VI) onto spent grain at $29 \pm 2^\circ\text{C}$ and $\text{pH} = 2$ of Cr(VI) solutions: 25 mg/L (■); 50 mg/L (●), and 100 mg/L (▲).

on the uptake of Cr(VI) by a nonliving biomass of water hyacinth root, and by Findon et al.¹¹ in their investigation of the sorption of Cu(II) by chitosan.

Sorption Isotherm

The equilibrium data for the sorption of Cr(VI) on spent grain at $29 \pm 2^\circ\text{C}$ at $\text{pH} 2$ could be fitted

into a modified Langmuir isotherm model of the form:

$$C_e N_e + (1/N^*b) + (C_e/N^*)$$

where C_e is the equilibrium concentration of the Cr(VI) solution (mg/L); N_e and N^* are, respectively, the amount sorbed at equilibrium and

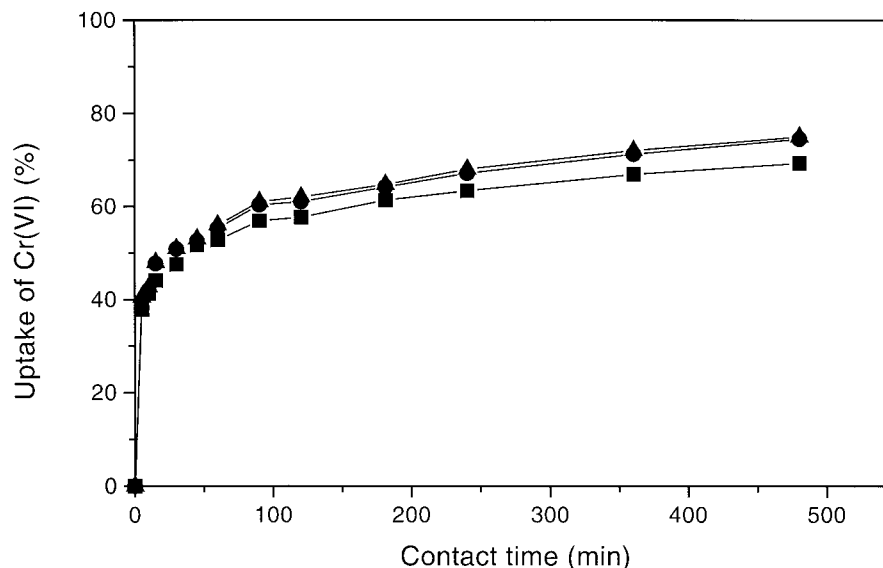


Figure 4 Effect of agitation on the uptake of Cr(VI) by spent grain: 100 rpm (■), 150 rpm (●), and 200 rpm (▲).

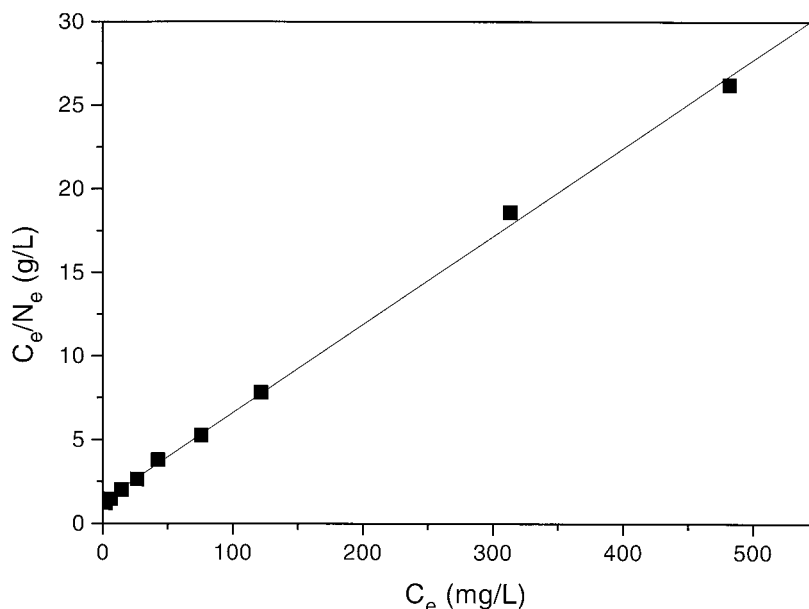


Figure 5 Langmuir isotherm for the Cr(VI)-spent grain system at $29 \pm 2^\circ\text{C}$.

maximum sorption capacity of spent grain (mg/g); and b is a constant related to the energy of sorption. A plot of C_e/N_e versus C_e is shown in Figure 5. From the slope of the graph the value of N^* was calculated to be 18.94 mg/g. This value compares favorably with values reported by Sharma and Forster⁶ for sugar beet pulp, maize cob, and sugar cane bagasse (13.4–17.2 mg/g) at pH 1.5–2.0.

Effect of Dosage

Figure 6 shows the uptake and sorption density of Cr(VI) as a function of dosage. The amount of Cr(VI) sorbed increased, whereas the sorption density decreased with increasing dosage. The nonlinearity of the sorption curve shows that the sorption process would be more efficient with

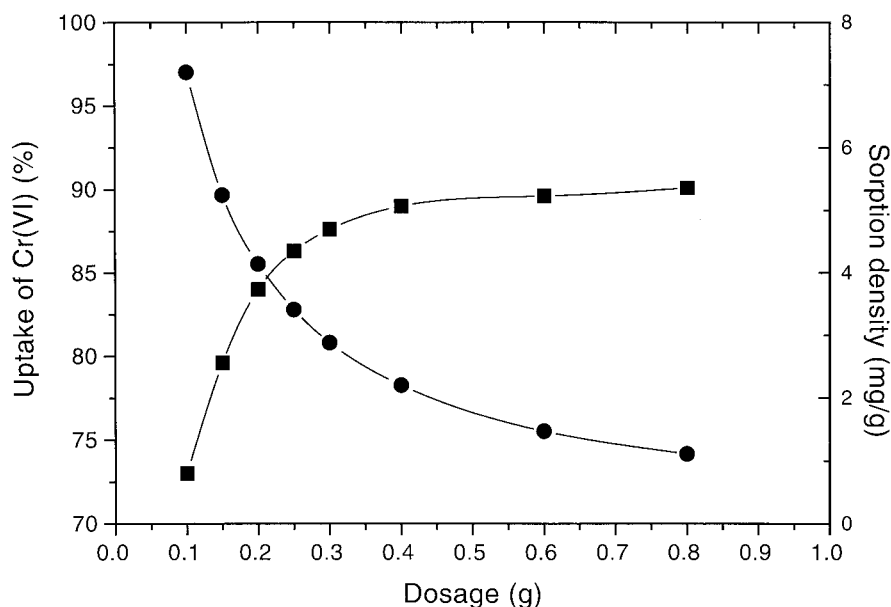


Figure 6 Uptake (■) and sorption density (●) of Cr(VI) by spent grain as a function of dosage.

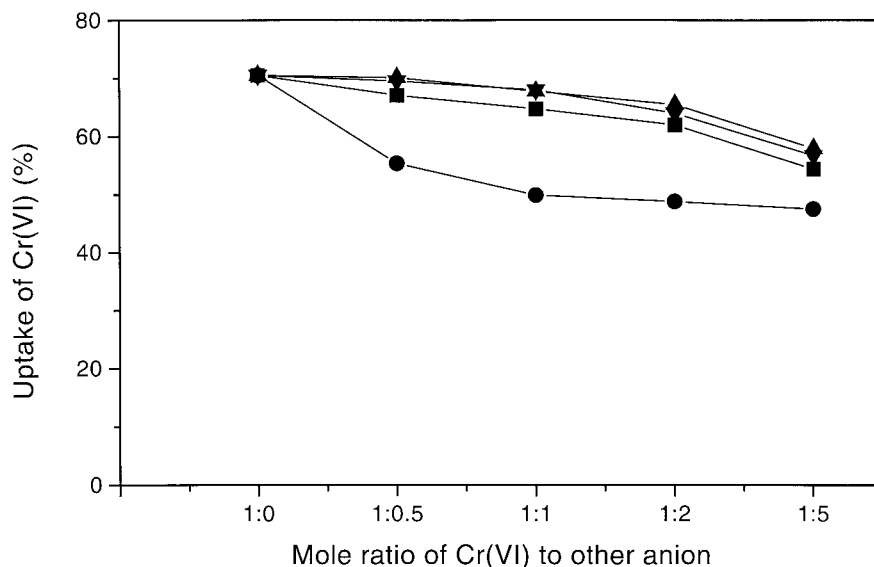


Figure 7 Effect of anion on the uptake of Cr(VI) by spent grain: phosphate (▲), nitrate (▼), arsenate (■), and sulfate (●).

multiple dosages than with a single large dosage. The initial 0.1 g could remove 73% of the initial Cr(VI), whereas the next 0.1 g could sorb an additional 12%, indicating a diminishing return of uptake with increasing dosage. Similarly, the sorption density decreased from 7.20 to 4.14 mg/g from a dosage of 0.1 to 0.2 g of spent grain. Such a study is useful to establish the optimum use of spent grain in the removal of Cr(VI) from an aqueous solution.

Effect of Other Anions in the Uptake of Cr(VI)

The presence of anions can have one of three effects on Cr(VI) uptake: (1) synergistic, (2) antagonistic, and (3) noninteractive. Figure 7 shows the effect of various anions on the sorption of Cr(VI) by spent grain. It is clear that all the anions studied showed an antagonistic effect. Sulfate ions had the greatest suppressing effect. It reduced the uptake from 70.5 to 47.5% when the molar ratio increased from 1:0 to 1:5. Hence, caution must be taken when applying spent grain in the removal of Cr(VI) in electroplating discharge and wood preservative waste, both of which contain sulfate ions. The same phenomenon was also reported by Low et al.⁴ in the study of Cr(VI) uptake by quaternized rice hull where NO_3^- , PO_4^{3-} , and AsO_4^{3-} showed similar suppressing effects.

Comparative Study on the Uptake of Cr(VI)

Table I shows the sorption of Cr(VI) by different sorbents under similar conditions. Activated car-

bon and synthetic anion exchanger exhibit the highest sorption. Chemically modified coconut husk, rice husk, and wood show uptakes similar to that of spent grain (73–80%). Bleaching earth had very little affinity for Cr(VI) (3%).

Application to Chrome-Plating Waste

A sample of chrome waste containing 50.67 mg/L Cr(VI) after treatment with spent grain at a pH value of 2.7 was reduced to 24.31 mg/L, indicating the effectiveness of spent grain as a sorbent for Cr(VI). Under similar conditions with a synthetic Cr(VI) solution the final concentration would be 12.75 mg/L. This confirms the early finding that the presence of other anions suppresses the uptake of Cr(VI).

Table I Update of Cr(VI) by Different Sorbents

Sorbent	Uptake ^a (%)
Bleaching earth	3.1
Moss	36.1
Wood	39.5
Hair	54.4
Chitin	56.7
Quaternized wood	73.2
Spent grain	74.5
Quaternized rice hull	78.3
Dye-coated coconut husk	79.6
Anion exchanger	91.1
Activated carbon	97.4

^a Conditions: 0.1 g of sorbent in 20 mL of 50 mg/L Cr(VI).

CONCLUSIONS

It was demonstrated that spent grain, a brewery by-product, could be used to remove or reduce Cr(VI) from both synthetic solution and chrome waste. Its full potential, however, can be realized only after a continuous flow study has been explored. Such a study is currently being undertaken.

The authors thank MPKSN for the financial support of this work through IRPA Grant No. 09-0204-0061.

REFERENCES

1. Bailey, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. D. *Water Res* 1999, 33, 2469.
2. Nourbakhsh, M.; Sag, Y.; Ozer, D.; Aku, Z.; Kutsal, T.; Caglar, A. *Process Biochem* 1994, 29, 1.
3. Kratochvil, D.; Pimentel, P.; Volesky, B. *Environ Sci Technol* 1998, 32, 2693.
4. Low, K. S.; Lee, C. K.; Ng, A. Y. *Bioresour Technol* 1998, 68, 205.
5. Sharma, D. C.; Forster, C. F. *Water Res* 1993, 27, 1200.
6. Sharma, D. C.; Forster, C. F. *Bioresour Technol* 1994, 47, 257.
7. Lagergren, S. *K Sven Vetenskapsakad Handl* 1898, 24, 1.
8. Grosset, T.; Trancart, J. L.; Thevont, D. R. *Water Res* 1986, 20, 21.
9. Ho, Y. S.; McKay, G. *Water Res* 2000, 34, 735.
10. Low, K. S.; Lee, C. K.; Ng, A. Y. *Int J Environ Stud* 1997, 53, 87.
11. Findon, A.; McKay, K.; Blair, H. S. *J Environ Sci Health* 1993, A28, 173.