Asian Journal of Chemistry; Vol. 26, No. 19 (2014), 6579-6582

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16638

Adsorption Behavior of Malachite Green from Aqueous Solution onto Bamboo Leaves Biomass

HONGMEI CHEN[1,*], LIPING ZHANG[1], XIANZHONG CHENG[1], SIQING CHENG[1] and DAZHONG YAN[2]

[1]School of Chemical and Environmental Engineering, Wuhan Polytechnic University, Wuhan 430023, Hubei Province, P.R. China
[2]School of Biology and Pharmaceutical Engineering, Wuhan Polytechnic University, Wuhan 430023, Hubei Province, P.R. China

*Corresponding author: Tel: +86 27 83943956, E-mail: chhmei15@163.com; whcxz502@163.com

Received: 5 November 2013; *Accepted*: 13 January 2014; *Published online*: 16 September 2014; AJC-15965

The native bamboo leaves biomass was investigated systematically as biosorbent for adsorption of malachite green from aqueous solution. The results show that the rapid malachite green absorption in aqueous solution by bamboo leaves biomass at pH 6 at ambient temperature observes the pseudo-second order reaction kinetics. The absorption isothermal behavior could be dissected well by Langmuir absorption isothermal, indicative of malachite green adsorbed in homogeneous surface of bamboo leaves biomass. The monolayer adsorption process for malachite green adsorption by bamboo leaves biomass and adsorption of each malachite green molecule with equal activation energy. This might be attributed to the unique morphology and composition of bamboo leaves biomass.

Keywords: Bamboo leaves biomass, Malachite green, Adsorption, Isotherm, Kinetics.

INTRODUCTION

Malachite green, a triphenylmethane dye and non-volatile compound, has been expressively prohibited in some countries to use in aquaculture industry as a strong antifungal, antibacterial and antiparasitical agent in fish farming[1,2] due to its high residue, highly toxic, teratogenic, carcinogenic, mutagenic, *etc*[3]. However, it is still used due to its low price, ready availability and bactericidal effect on fungus diseases prevention and control[4], which might enter into the food chain and cause carcinogenic and mutagenic for aquatic organisms[5]. As such, it is extremely important to develop methods for malachite green removal from waste effluents based on an environmental point of view.

Nowadays, it is well known that biosorption with biomaterial as sorbent is very efficient and relatively inexpensive method for dye and metal contaminant removal owing to its simple operation, low cost, wide material source without any secondary pollution. Thus, a large number of biomaterials have been utilized as absorbent for contaminant removal, such as chitosan[6], yeast cell[7], husk leaf[8], sugarcane bagass[9], rice husk[10], oil palm fibers[11], lemon peel[12], sawdust[13-15], agricultural by-product[16-18] and hen feathers[19] *etc*. Among these, bamboo leaves biomass is a potentially attractive biosorbent owing to its rich natural resource in the world. It mainly consists of cellulose, hemicellulose, lignin and polyphenol[20,21] with many different of surface functional groups such as alcohols, aldehydes, carboxylic acids, ketones and phenolic hydroxides[22]. Therefore, bamboo leaves biomass has been extensively applied to the extraction of antioxidant[18,23], flavonoids[24], polysaccharides and hemicelluloses preparation[21,22], pozzolanic material[25,26]. However, to our best of knowledge, no study has been carried out using natural bamboo leaves biomass for malachite green removal *via* adsorption.

In the present study, bamboo leaves biomass was used as biosorbent for malachite green removal *via* adsorption from aqueous solution and the malachite green adsorption behavior by bamboo leaves biomass was investigated under variable systematic parameters using Langmuir and Freundlich sorption isotherms. The experimental results demonstrate that bamboo leaves biomass as ecofriendly and inexpensive biosorbent is potential for malachite green removal from aqueous solution.

EXPERIMENTAL

Fresh bamboo leaves biomass were collected from a local farm in Xinzhou district (Wuhan, China), malachite green was purchased from Shanghai Chemical Reagent Company (China) without purification when used. All other reagents and solvents were of analytical grade otherwise specified.

General procedure: The collected bamboo leaves biomass were washed repeatedly with distilled water to remove dust and soluble impurities, allowed to air-dry in the sun and then dried further in an oven at 75 °C for 12 h. The resulting sample was crushed into a fine powder by a pulverizing machine (Joyoung, China) and then sieved to pass through a 100 mesh screen. The bamboo leaves biomass powder was kept in a glass bottle for further use.

The stock solution of malachite green containing 500 mg L^{-1} was prepared by dissolving accurately weighed 1 g of malachite green with 250 mL of distilled water and then quantifying to 500 mL volumetric flask. The solution pH was adjusted with 0.1 mol L^{-1} NaOH or HCl solutions using a Thermo 868 pH meter (Thermo Orion Corporation, America) supplied with a combined glass electrode.

Detection method: The composition of the as-prepared bamboo leaves biomass was determined by FT-IR spectrometer (Nicolet AVATAR 330 FTIR; Thermo Electron Corporation, Madison, WI, USA). The morphology of bamboo leaves biomass powder was evaluated by a JEOL-2100F scanning electron microscope (Japan) with the accelerating voltage of 200 kV.

Malachite green adsorption experiments were performed using a batch equilibrium technique by placing 0.10 g of bamboo leaves biomass in a 100 mL conical flask containing 50 mL of malachite green solution at various initial concentrations and equilibrating on a thermostatic shaker (Tongzhou Instrument Plant, China) with a speed of 200 rpm. At desirable time interval, the sample solution was withdrawn and centrifuged by a TDL40B centrifuge (Anke Instrument Plant, China) at 3000 rpm for 10 min and then, the concentration of remaining malachite green was determined at 618 nm by the spectrophotometer (Thermo Spectronic, USA). The removal efficiency (R %) and the adsorption capacity(q_e, mg g^{-1}) of malachite green by bamboo leaves biomass was calculated by using eqn.(1) and (2), respectively.

$$R\ \% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

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

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of malachite green in solution, respectively, m (g) the mass of bamboo leaves biomass and V (L) the volume of malachite green solution.

RESULTS AND DISCUSSION

Optimization of malachite green absorption condition in aqueous solution by bamboo leaves biomass: The solid-liquid adsorption is a complicated system depending on adsorbent, adsorbate, solution pH, temperature, pressure, *etc*. Thus, the optimization of absorption condition is crucial for investigating the solid-liquid adsorption behavior.

Fig. 1 shows the effects of solution pH and initial malachite green concentration on malachite green removal efficiency or malachite green absorption capacity at fixed experimental condition. Firstly, solution pH plays a very important role on malachite green adsorption in aqueous solution by bamboo leaves biomass. As shown in Fig. 1a for malachite green removal efficiency from solution by bamboo leaves biomass as a function of pH with malachite green initial concentration of 50 mg L^{-1} and 60 min equilibrium time at ambient temperature, malachite green removal efficiency increases remarkably with increasing pH up to pH 6, at which malachite green adsorption nearly reaches the adsorption saturation. This may be due to the composition of absorbent bamboo leaves biomass because solution pH may affect both aqueous chemistry and surface binding-sites of the absorbent[27]. As shown in Fig. 2a, the FT-IR spectrum of bamboo leaves biomass reveals that there exist many carboxyl and hydroxyl groups on the surface of bamboo leaves biomass. As such, the protonation-deprotonation equilibrium of bamboo leaves biomass in aqueous solution is affected greatly by solution pH to impact further the cationic malachite green absorption[28]. Therefore, pH 6 is thought to be the optimum pH for malachite green adsorption in aqueous solution by bamboo leaves biomass at ambient bamboo leaves biomass temperature. On the other hand, the initial absorbate concentration is very important parameter for adsorption behavior of solid-liquid adsorption as well because it provides an important driving force to overcome the resistances of mass transfer off all molecules between aqueous phase and solid phase[29]. As shown in Fig. 1b for the initial malachite green concentration dependence of malachite green removal efficiency at pH 6 and ambient temperature, it was observed that malachite green removal efficiency by bamboo leaves biomass tended to decrease slightly from 97.6 to 94.8 % with the initial malachite green concentration from 10 to 50 mg L^{-1} and then decreased markedly to 54.6 % with the initial malachite green concentration up to 150 mg L^{-1}. This might result from the morphology of the absorbate bamboo leaves biomass, as shown in Fig. 2b for SEM image of bamboo leaves biomass. It was found that the rough and irregular surface of bamboo leaves biomass has considerable number of pores, which result in suitable binding site for malachite green. As such, at low initial malachite green concentration, the binding sites are enough to accommodate malachite green and thus malachite green removal efficiency is quite high, while at high initial malachite green concentration, malachite green reaches accommodation saturation. This is verified further by initial malachite green concentration dependence of malachite green adsorption capacity. Fig. 1c showed that the malachite green adsorption capacity increases with initial malachite green concentration and when initial malachite green concentration is up to 100 mg L^{-1}, malachite green adsorption reach saturation. So, 100 mg L^{-1} is thought to be the suitable initial malachite green concentration at pH 6 and ambient temperature.

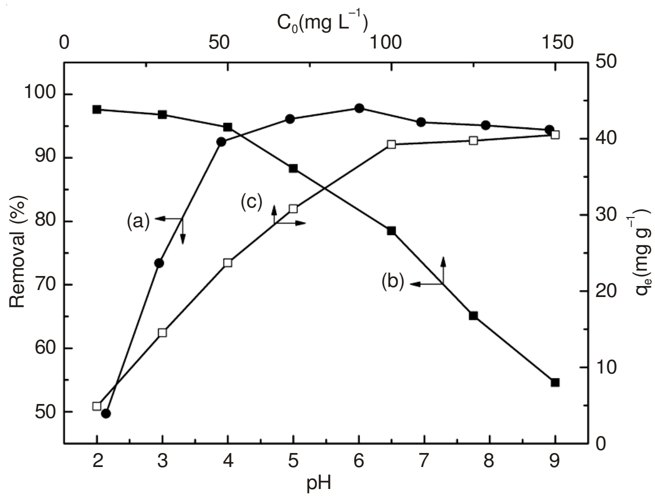

Fig. 1. Malachite green removal efficiency and adsorption capacity dependence of pH (a), initial malachite green concentration (b, c) for equili-brating time 90 min at ambient temperature. a: C_0 = 50 mg g^{-1}. b, c: pH 6

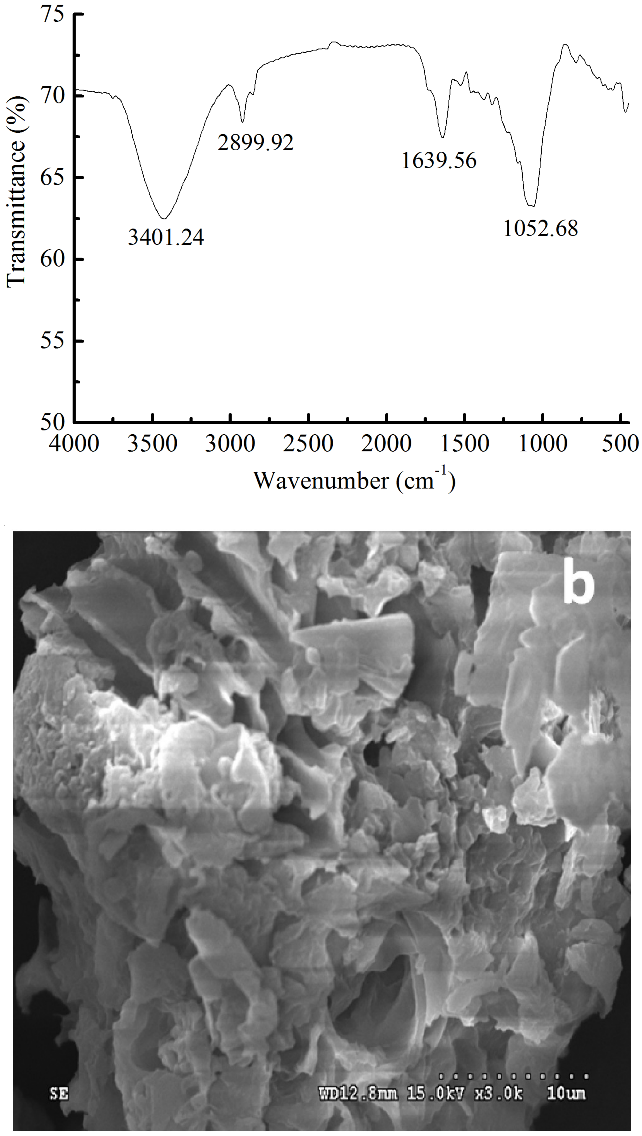

Fig. 2. FT-IR spectrum (a) and SEM image (b) of bamboo leaves biomass

Thermodynamics and kinetics of malachite green absorption in aqueous solution by bamboo leaves biomass: Generally, the solid-liquid adsorption is dependent on temperature. However, for malachite green adsorption in aqueous solution by bamboo leaves biomass investigated in this work, the temperature has no appreciable effect on malachite green removal efficiency (not shown here), which was also observed by Sun *et al.*[30] for the biosorption of dyes onto biomass. Therefore, it is potential for implementation of the industrialization for absorbent bamboo leaves biomass powder to enable to operate at ambient temperature.

Malachite green adsorption capacity by bamboo leaves biomass as a function of time was carried out at different initial malachite green concentration at pH 6 at ambient temperature. It was shown that malachite green absorption by bamboo leaves biomass is very rapid to reach absorption equilibrium in nearly 60 min. The experimental results were fitted the kinetic Eqn. (3) and (4) with respect to pseudo-first order and pseudo-second order reactions, respectively (Fig. 3). It can be seen that the pseudo-second order kinetic equation is fitted better than the pseudo-first order one for malachite green adsorption

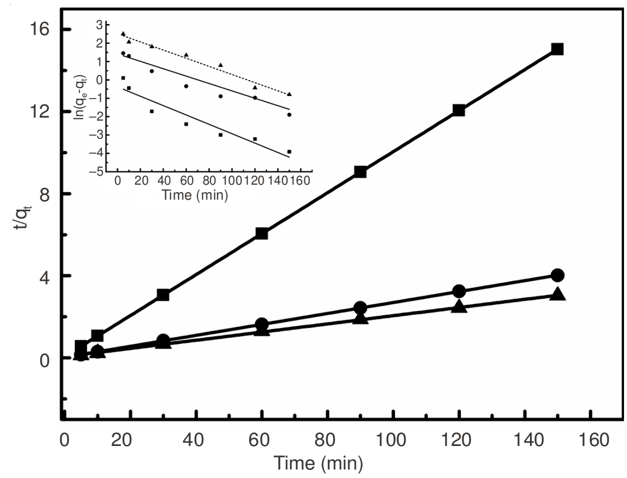

Fig. 3 Fitted kinetic curves with respect to pseudo-second order reaction for malachite green adsorption in aqueous solution by bamboo leaves biomass with initial malachite green concentration of 20 mg g^{-1} (■), 75 mg g^{-1} (●), 100 mg g^{-1} (▲) at pH 6 and ambient temperature. Inset: the fitted kinetic curves with respect to pseudo-first order reaction

by bamboo leaves biomass with the coefficient of determination (R^2) of more than 0.9999. The calculated equilibrium adsorption capacity from pseudo-second-order kinetics is 49.25 mg g^{-1}, which is very close to the saturation adsorption capacity (40 mg g^{-1}) in Fig. 1c.

$$\ln (q_e-q_t) = \ln q_e-k_1t \quad (3)$$

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}t \quad (4)$$

where t (min) is time, q_e and q_t (mg g^{-1}) are the adsorption capacity at equilibrium and at time *t*, respectively and k_1 (min^{-1}) and k_2 (mg g^{-1} min^{-1}) are the first-order and second order rate constants, respectively.

Adsorption isotherm for malachite green adsorption in aqueous solution by bamboo leaves biomass: Two general isothermal adsorption models, Langmuir and Freundich models were used for the analyses of malachite green adsorption by bamboo leaves biomass. Langmuir model is based on the assumption of monolayer adsorption on homogeneous surface[31], while Freundlich model is an empirical model and assumed to heterogeneous adsorption with uniform energy, which are expressed in Eqn. (5) and (6), respectively.

$$\frac{t}{q_e}=\frac{1}{Q_0}+\frac{1}{K_LQ_0C_e} \quad (5)$$

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (6)$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e (mg L^{-1}) is the adsorbate equilibrium concentration remained in the solution, Q_o is the maximum adsorption capacity, K_L and K_f (L mg^{-1}) are Langmuir and Freundlich constants, respectively, which are related to the energy of adsorption and 1/n is the heterogeneity factor.

Fig. 4 presents Langmuir and Freundlich adsorption isothermal for malachite green adsorption in aqueous solution by bamboo leaves biomass with initial malachite green concentration of 100 mg L^{-1} at pH 6 at ambient temperature. It can be seen that Langmuir adsorption isothermal is fitted better to the

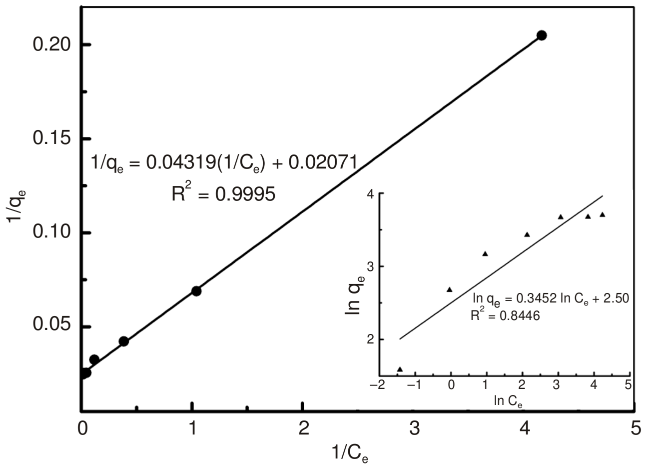

Fig. 4. Langmuir adsorption isotherm for malachite green adsorption in aqueous solution by bamboo leaves biomass at pH 6 and ambient temperature with initial malachite green concentration of 100 mg g^{-1}. Inset: Freundich adsorption isotherm

experimental data with fitting coefficient of determination (R^2) of 0.9995 than the Freundlich one with fitting coefficient of determination (R^2) of 0.8446, representing malachite green adsorption in aqueous solution by bamboo leaves biomass as Langmuir isothermal adsorption. Therefore, malachite green adsorption in aqueous solution by bamboo leaves biomass takes place in homogeneous surface of sorbent, the adsorption process is monolayer and adsorption of each malachite green molecule has equal activation energy. Based on Langmuir adsorption isothermal, the maximum equilibrium adsorption capacity was estimated to be 48.3 mg g^{-1}, which is in agreement with that based on the kinetic equation above. This further corroborates the reliability of the experimental results.

Conclusion

In present study, malachite green adsorption behavior in aqueous solution by the native bamboo leaves biomass has been investigated systematically. The rapid malachite green absorption by bamboo leaves biomass in aqueous solution at pH 6 necessitates only 1 h to reach equilibrium and could be operated at ambient temperature, which is attributed to the morphology and composition of bamboo leaves biomass. The malachite green adsorption kinetics in aqueous solution by bamboo leaves biomass observes the pseudo-second order reaction and the adsorption isotherms of malachite green onto bamboo leaves biomass could be interpreted by Langmuir adsorption isotherm with a monolayer adsorption capacity of 48.3 mg g^{-1}, indicating the malachite green adsorbed in homogeneous surface of bamboo leaves biomass, the malachite green monolayer adsorption process and adsorption of each molecule with equal activation energy. Therefore, the native bamboo leaves biomass is potential in efficient removal of malachite green from aqueous solution due to its low cost, ease-handling and environmental friendliness.

ACKNOWLEDGEMENTS

This work was supported by the Hubei Provincial Natural Science Foundation in China (No.2008CDA100) and the National Natural Science Foundation of China (No. 60736042, 31270112).

REFERENCES

1. Z. Bekci, Y. Seki and L. Cavas, *J. Hazard. Mater.*, **161**, 1454 (2009).
2. A.N. Kagalkar, M.U. Jadhav, V.A. Bapat and S.P. Govindwar, *Bioresour. Technol.*, **102**, 10312 (2011).
3. K.-H. Hu and M. Meng, *Asian J. Chem.*, **25**, 5827 (2013).
4. E. Sudova, J. Machova, Z. Svobodova and T. Vesely, *Vet. Med.*, **52**, 527 (2007).
5. D. Zhao, Y. Ding, S. Chen, T. Bai and Y. Ma, *Asian J. Chem*, **25**, 5756 (2013).
6. D.Y. Pratt, L.D. Wilson and J.A. Kozinski, *J. Colloid Interf. Sci.*, **395**, 205 (2013).
7. A. Singh, Manju, S. Rani and N.R. Bishnoi, *Ecol. Eng.*, **47**, 291 (2012).
8. A.A. Jalil, S. Triwahyono, M.R. Yaakob, Z.Z. Azmi, N. Sapawe, N.H. Kamarudin, H.D. Setiabudi, N.F. Jaafar, S.M. Sidik, S.H. Adam and B.H. Hameed, *Bioresour. Technol.*, **120**, 218 (2012).
9. A.A. Kadam, H.S. Lade, S.M. Patil and S.P. Govindwar, *Bioresour. Technol.*, **132**, 276 (2013).
10. S. Chowdhury, R. Mishra, P. Saha and P. Kushwaha, *Desalination*, **265**, 159 (2011).
11. M.S. Sajab, C.H. Chia, S. Zakaria and P.S. Khiew, *Bioresour. Technol.*, **128**, 571 (2013).
12. K.V. Kumar, *Dyes Pigments*, **74**, 595 (2007).
13. S.D. Khattri and M.K. Singh, *J. Hazard. Mater.*, **167**, 1089 (2009).
14. A. Witek-Krowiak, *Chem. Eng. J.*, **171**, 976 (2011).
15. H. Zhang, Y. Tang, X. Liu, Z. Ke, X. Su, D. Cai, X. Wang, Y. Liu, Q. Huang and Z. Yu, *Desalination*, **274**, 97 (2011).
16. R. Ahmad and R. Kumar, *J. Environ. Manage.*, **91**, 1032 (2010).
17. B.H. Hameed and M.I. El-Khaiary, *J. Hazard. Mater.*, **154**, 237 (2008).
18. Y. Zhang, Y. Jiao, C. Liu, X. Wu and Y. Zhang, *Food Chem.*, **107**, 1326 (2008).
19. M.A. Khosa, J. Wu and A. Ullah, *RSC Adv.*, **3**, 20800 (2013).
20. Q. Luo, H. Peng, M. Zhou, D. Lin, R. Ruan, Y. Wan, J. Zhang and Y. Liu, *BioResources*, **7**, 5817 (2012).
21. H. Peng, N. Wang, Z. Hu, Z. Yu, Y. Liu, J. Zhang and R. Ruan, *Ind. Crops Prod.*, **37**, 41 (2012).
22. H. Peng, M. Zhou, Z. Yu, J. Zhang, R. Ruan, Y. Wan and Y. Liu, *Carbohydr. Polym.*, **95**, 262 (2013).
23. J. Xie, Y.-S. Lin, X.-J. Shi, X.-Y. Zhu, W.-K. Su and P. Wang, *Ind. Crops Prod.*, **43**, 276 (2013).
24. Y. Zhang, J. Shen, Z. Yu, B. Lu and D. Lou, *Chem. Ind. Forest Prod.*, **24**, 95 (2004).
25. V.N. Dwivedi, N.P. Singh, S.S. Das and N.B. Singh, *Int. J. Phys. Sci.*, **1**, 106 (2006).
26. E. Villar-Cociña, E.V. Morales, S.F. Santos, H. Savastano Jr. and M. Frías, *Cement Concr. Compos.*, **33**, 68 (2011).
27. C.X. Cheng, Y.C. Hou, B. Li and W.Z. Yi, *Asian J. Chem.*, **25**, 367 (2013).
28. S. Arellano-Cárdenas, S. López-Cortez, M. Cornejo-Mazón and J.C. Mares-Gutiérrez, *Appl. Surf. Sci.*, **280**, 74 (2013).
29. A.S. Bhatt, P.L. Sakaria, M. Vasudevan, R.R. Pawar, N. Sudheesh, H.C. Bajaj and H.M. Mody, *RSC Adv.*, **2**, 8663 (2012).
30. L. Sun, S. Wan and W. Luo, *Bioresour. Technol.*, **140**, 406 (2013).
31. A. Simi and V. Azeeza, *Asian J. Chem.*, **22**, 4371 (2010).