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Investigation of acid black 1 adsorption onto amino-polysaccharides

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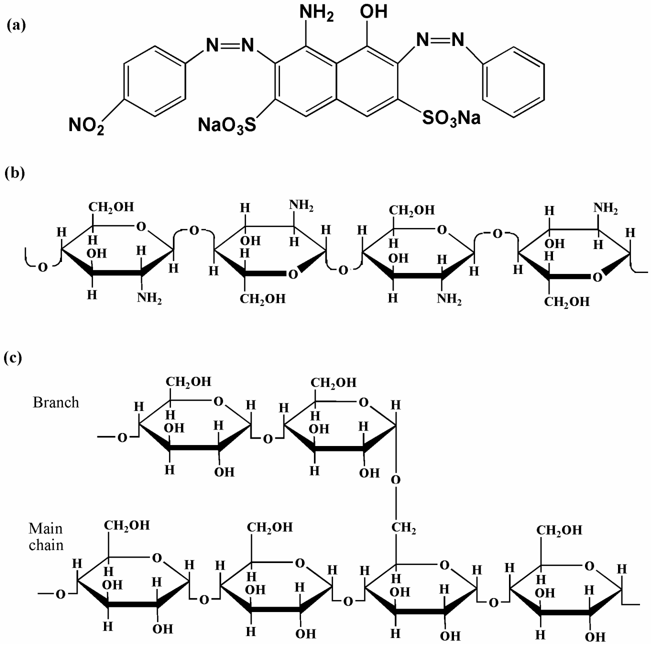
Summary

Chitosan and four cross-linked amino-starches (CAS) were employed to remove the acid dye acid black 1 (C. I. 20470) from aqueous solution. The optimum initial pH value is 3.0 and the adsorptions reach equilibrium after 3h. To describe the interactions of acid black 1 with different amino-polysaccharides, the linearized Langmuir and Freundlich isotherms were tested to fit the experimental data. The results indicate that the best-fit model is Langmuir isotherm and the mechanism is based on electrostatic attraction. The adsorption capacity of chitosan is highest amongst the amino-polysaccharides examined. The FT-IR spectra suggest that the amino groups of polysaccharides are protonated and the acid black 1 molecules were effectively adsorbed.

Introduction

With the development of textile and related industries, dyeing effluents cause serious environmental problem [1, 2]. Many of the dyestuffs are toxic and carcinogenic [3, 4], consequently the treatment of dyeing effluents has long been a major concern. Several treatment technologies for dye removal have been investigated extensively, such as chemical oxidation [5, 6], photodegradation processes [7], activated sludge [8, 9] and adsorption procedures [10-13]. Fragments are always produced and remained in effluents by using techniques that change or destroy the dye chromophore. Comparatively, adsorption of dye molecules onto a substrate (adsorbent) can be a very effective and low-cost method [14-16]. Proper selection of adsorbent using in the adsorption procedure will produce high-quality treated effluents. Recently natural polysaccharides are tested in treatment of dye effluent [17]. Amongst numerous polysaccharides starch is an abundant, inexpensive, renewable and fully biodegradable natural raw material. However, it shows a very low effect on adsorption of dyes [17]. While another abundant polysaccharide, chitosan presents a high capacity for many dyes compared to many polysaccharides without amino group [18-20]. Therefore the amino group may be important for polysaccharides in adsorption of dye molecules [21]. In this paper, four cross-linked amino-starches (CAS) were synthesized by using ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine, respectively. The purpose is to investigate their interactions with acid dye molecule using acid black 1 (C. I. 20470), in an attempt to find out the difference of adsorption abilities of CAS and chitosan. The FT-IR spectra are also discussed. The chemical structure of acid black 1 (AB1), chitosan and starch is presented in Scheme 1.



Scheme 1. Chemical structure of acid black 1(a), chitosan (b) and starch (c).

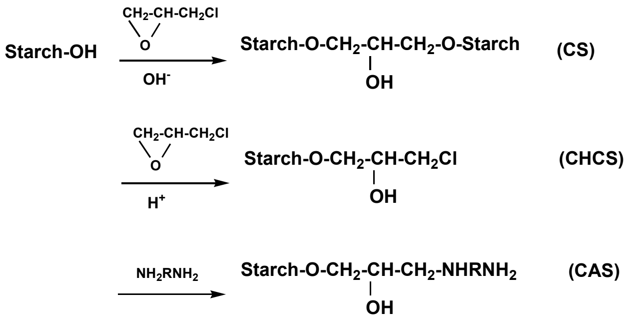
Experimental Section

Materials

Chitosan was supplied by the Nantong Shuanglin Ltd. Co., China. The deacetylizaton of chitosan is over 95%. Commercial maize starch, food grade quality, was used in this research. Acid black 1 (C. I. 20470) was purchased from Sigma chemical company. Epichlorohydrin, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and other routine reagents were analytical grade. They were used without any further purification process.

Preparation of cross-linked amino-starch (CAS)

The synthesis of cross-linked amino-starch was according to literature [22]. The procedure is depicted in Scheme 2. Firstly the cross-linked starch (CS) was synthesized by reacting 100g maize starch with 8.0mL epichlorohydrin (ECH) in 200mL dilute NaOH solution (0.16mol•L^{-1}) under 25°C. After 18h, the pH was adjusted to 6-7 and the CS was separated from solution. Then the intermediate, 3-chloro-2-hydroxypropyl cross-linked starch (CHCS) was prepared from 25g of dried CS with ECH in the presence of 60% $HClO_4$ (the molar ratio was CS: ECH : $HClO_4$ = 1:2.5:0.03). The dried CHCS further reacted with acyclic polyamine to produce cross-linked amino-starch (CAS) in basic solution under 60°C for 8h. The product was washed with deionized water, dilute HCl solution, dilute NaOH solution and acetone in sequence. The acquired CAS was kept in a vacuum oven for 1 day and stored in desiccators. CAS1, CAS2, CAS3 and CAS4 were synthesized using ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine, respectively. The nitrogen content was measured on a Vario EL III elemental analyzer. The proportions of nitrogen are 0.81, 0.96, 1.27, 1.51, 8.11% for CAS1, CAS2, CAS3, CAS4 and chitosan, respectively.



Scheme 2. The reaction process of cross-linked amino-starch (CAS)

Equipments

The concentration of AB1 in aqueous solution was determined using a Agilent 8453 UV-Vis spectrophotometer. The absorbance was measured over a range from 300 to 800nm. Absorbance values at the wavelength of maximum absorbance (λ_{max}) were recorded, and AB1 solution was initially calibrated for concentration in terms of absorbance units. Fourier transform infrared spectra were recorded on Bruker vector 22 spectrometer with KBr pellets in the 4000-400cm^{-1} regions.

Sorption experiments

Sorption studies were performed by the batch technique. The effect of initial pH was observed by studying the adsorption of AB1 over a pH range of 2-9. For these experiments, a series of 100mL conical flasks were employed. Each flask was filled with 50 mL of AB1 solution having a concentration of 600$mg\cdot L^{-1}$ at varying initial pH. For equilibrium sorption studies, a fixed mass of amino-polysaccharide (0.0500g) was weighed into flasks and contacted with 50mL of AB1 solutions with predetermined initial concentrations (varied from 600$mg\cdot L^{-1}$ to 3000$mg\cdot L^{-1}$). The initial pH of the solutions was adjusted to 3.0. Then the flasks were sealed and agitated for 24h at 200 rpm in the thermostatic shaker bath. The temperature was maintained at 25±1°C. After filtration, the concentrations of AB1 solutions were determined.

Results and discussion

Influence of the initial pH on the adsorption capacity

The influence of initial pH on the adsorption capacity was observed by studying over a pH range of 2-9. The wavelength of maximum absorbance (λ_{max}) of AB1 was 618nm, and it did not shift at varied pH values. The concentrations of AB1 solutions were measured at the wavelength of 618nm. The initial concentration of AB1 is 600mg•L^{-1}. The results show that maximum removal is achieved in acidic condition for different amino-polysaccharides (Figure 1). With the increase of pH value, the removal percentage decreases. These facts suggest that the interaction of amino-polysaccharide with AB1 is based on electrostatic attraction. In aqueous solution, AB1 is first dissolved and the sulfonate groups dissociate and are converted to anionic ions. Also, in the presence of H$^+$, the amino groups of polysaccharides become protonated. Then the adsorption process is due to ionic interactions (for example -NH_3^+••• ^-O_3S-). Different CAS behaves closely and the lowest removal is about 50%. But the lowest removal of AB1 for chitosan reduces to about 10% at pH value 8.0. It is because that the cross-linked starch is amorphous and chitosan can form a certain crystal via the formation of hydrogen bonds between different macromolecular chains [23].

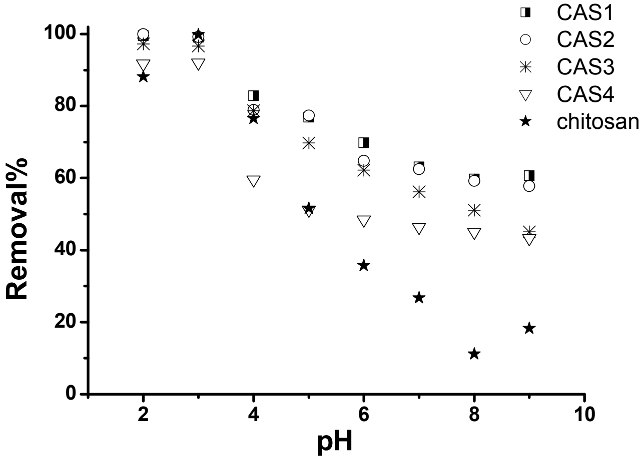


Figure 1. Effect of initial pH on the adsorption of AB1 by different amino-polysaccharides. The initial concentration of AB1 is 600mg•L^{-1}.

Effect on contact time

The effect of contact time on the adsorption of AB1 was also studied for different amino-polysaccharides, and the results are shown in Figure 2. The results indicate that equilibrium was achieved after 3h for different amino-polysaccharides. The rates of uptake of AB1 are rapid in the beginning and 50% of the ultimate adsorption occurs within the first hour of contact. But the effect of removal is different for various amino-polysaccharides. Chitosan shows a faster adsorption rate and a higher removal than the others.

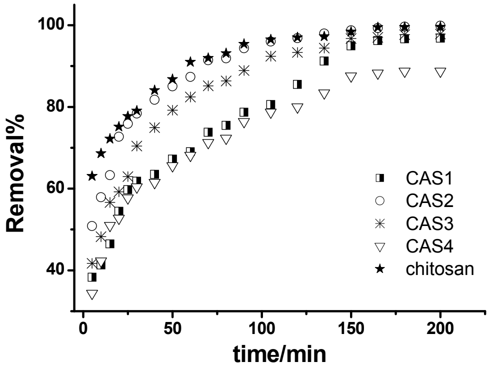


Figure 2. Effect of contact time on adsorption of AB1 by different amino-polysaccharides at the initial pH value 3.0. The initial concentration of AB1 is 600mg•L^{-1}.

Equilibrium isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents. It is of importance in optimizing the use of adsorbents. Equilibrium data were obtained by using batch technology described in experimental section at the optimum initial pH 3.0. Various types of adsorption isotherms (Langmuir and Freundlich) were tested to fit the experimental data. The well-known Langmuir isotherm originally proposed to describe the adsorption of gas molecules onto metal surfaces [24]. The model assumes uniform energies of adsorption onto the surface and no migration of adsorbate in the plane of surface. Moreover the Langmuir adsorption isotherm has successfully applied to many other real sorption courses of monolayer sorption, and its linear form is written as

$$\frac{c_e}{q_e} = \frac{1}{ab} + \frac{1}{a} c_e \qquad \textbf{(1)}$$

where q_e is the adsorbed amount of the dye at equilibrium, c_e is the adsorbate concentration at equilibrium in aqueous solution. The Langmuir isotherm parameters are a and b. The capacity of the adsorbent can be evaluated by a, and the parameter b includes various physical constants [25, 26]. The linearized Langmuir isotherm gives satisfying fit of equilibrium data for different amino-polysaccharides (Figure 3). Parameters of linear form of Langmuir isotherms (Equation 1) and the correlation coefficients (R2) are showed in Table1 for various amino-polysaccharides.

Another isotherm is Freundlich equation describing heterogeneous systems [27]. It is an empirical equation, and the linear form is as follows

$$\ln q_e = \ln K_f + \frac{1}{n} c_e \qquad \textbf{(2)}$$

where K_f is the Freundlich constant, and *1/n* is the heterogeneity factor. In this research the Freundlich equation is also employed to characterize the adsorption of AB1 onto various amino-polysaccharides (Figure 4).

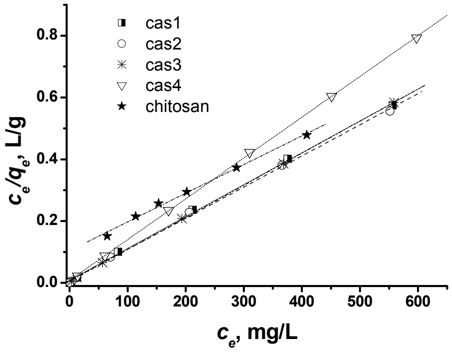


Figure 3. Linearized Langmuir isotherm for the adsorption of AB1 by various amino-polysaccharides.

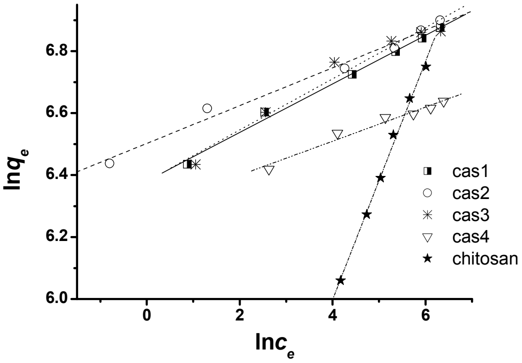


Figure 4. Linearized Freundlich isotherm for the adsorption of AB1 by various amino-polysaccharides.

The results show that the Langmuir isotherm is the best-fit model for the examined amino-polysaccharides and the Freundlich isotherm also gives acceptable fit (Table 2). It can be seen from Table 1 that the adsorption capacities of different amino-polysaccharides are in the order of chitosan > CAS2 > CAS1 > CAS3 > CAS4. Due to the mechanism is based on electrostatic force, the molecule of AB1 interacts with the protonated primary and secondary amine ($-NH_3^+\cdots{}^-O_3S-$ and $=NH_2^+\cdots{}^-O_3S-$) existing in amino-polysaccharides. Compared to CAS, chitosan is a linear polysaccharide [28] and has more primary amines resulting in a higher adsorption capacity. Although the nitrogen content increases from CAS1 to CAS4, the capacity of CAS4 is lowest. The chain length of polyamine is considerable. The molecular chain of tetraethylenepentamine is longest amongst the polyamine used. After it was grafted to starch to obtain CAS4, the branch chains of cross-linked starch elongate and the molecule become curled resulting in shielding of amine groups. It weakens the ionic interaction between CAS4 and AB1. Therefore the capacity of CAS4 is lowest. But the capacities of CAS2 and CAS1 are close to chitosan. Since starch is more abundant than chitosan, the cross-linked amino-starch should be obtained more conveniently. The synthsis of CAS is also simple and in high yield. Besides the amino-polysaccharides, some adsorbents for AB1 removal have been reported such as carbon and the magnetic brewer's yeast. However their capacities for AB1 are lower than the amino-polysaccharides. The unburned carbon has a capacity of 0.527 mmol•g^{-1} [29] and the modified magnetic brewer's yeast has a capacity of 11.6mg•g^{-1} for AB1 [30]. The very similar behaviors of the adsorbents for AB1 are the adsorption process that they can be described by Langmuir isotherm.

Table 1. Parameters of linearized Langmuir isotherm (Equation 1) of AB1 adsorption onto different amino-polysaccharides

adsorbent	a (mg•g^{-1})	b (L•mg^{-1})	R^2	capacity of adsorbent (mg•g^{-1})	capacity of adsorbent (mmol•g^{-1})
CAS1	970.87	0.117	0.9995	970.87	1.5748
CAS2	990.10	0.138	0.9993	990.10	1.6060
CAS3	961.54	0.225	0.9999	961.54	1.5597
CAS4	757.58	0.161	0.9999	757.58	1.2289
chitosan	1078.03	0.009	0.9975	1078.03	1.7487

Table 2. Freundlich isotherm (Equation 2) constants for AB1 adsorption onto different amino-polysaccharides

adsorbent	K_f (mg•g^{-1})(L•g^{-1})$^{1/n}$	n	R^2
CAS1	591.91	12.8	0.9972
CAS2	668.34	16.4	0.9928
CAS3	591.57	12.1	0.9811
CAS4	540.39	18.2	0.9844
chitosan	87.61	2.61	0.9976

Fourier transform infrared spectra

The different FT-IR spectra of chitosan before and after adsorption of AB1 are shown in Figure 5 in the region of 1800-600cm^{-1}. For chitosan, a broad peak at 1599 cm^{-1} is attributed to the δN-H out of plane vibration. The peaks at 1421, 1384 and 1325 cm^{-1} are assigned to the coupling of δO-H and δC-H vibration. Another important region is at the strong and broad peaks of 1160, 1130 and 1081 cm^{-1}, which causes by the coupling of νC-O, νC-N and νC-C in chitosan, respectively. After adsorption of AB1 in acid condition, the N-H out of plane vibration splits into two peaks at 1576 and 1540 cm^{-1} attributed to the $\delta_{as}NH_3^+$ and $\delta_sNH_3^+$, respectively [31]. The peaks at 1421 and 1384cm^{-1} remain showing the vibration of δO-H and δC-H. A newly moderate sharp peak at 1332 cm^{-1} indicates the νN=O vibration. The four peaks of 1635, 1493, 1285 and 1223 cm^{-1} are the characteristic νC=C vibration of aromatic rings. The strong and broard peaks at 1160, 1130 and 1081 cm^{-1} caused by the coupling of νC-O, νC-N and νC-C become sharper, due to incorporating the significant $\nu_{as}SO_2$ and ν_sSO_2 vibration [32]. Accordingly, the amino groups of chitosan are protonated and the AB1 molecules were effectively adsorbed onto chitosan. After AB1 adsorption on CAS, a similar trends were observed. As illustration of CAS2 in Figure 6, the N-H out of plane vibration splits into two peaks at 1613 and 1575 cm^{-1} attributed to the $\delta_{as}NH_3^+$ and $\delta_sNH_3^+$ vibration like presence in chitosan. The typical vibration of νN=O, $\nu_{as}SO_2$ and ν_sSO_2 are clearly observed at the peaks of 1336, 1150 and 1040 cm^{-1}, respectively. The characteristic four peaks of νC=C vibration of aromatic rings are identifiable.

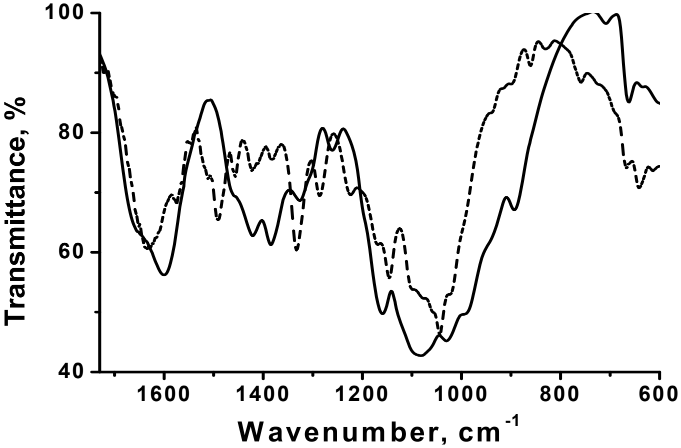


Figure 5. FT-IR spectra of chitosan (—) and chitosan with AB1 (-----)

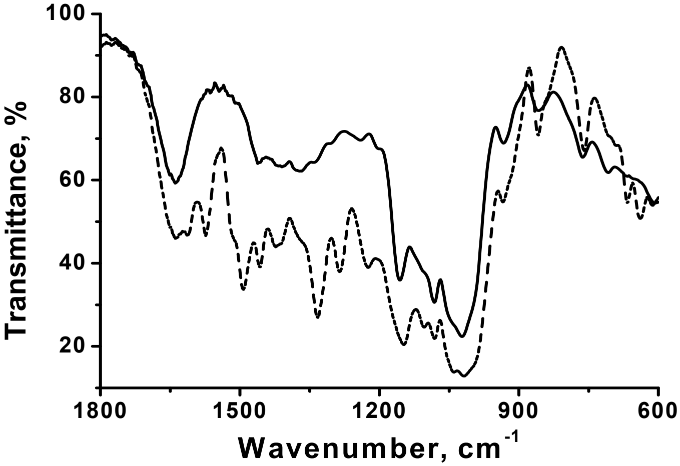


Figure 6. FT-IR spectra of CAS2 (—) and CAS2 with AB1 (-----).

Conclusions

Different acyclic polyamine modified cross-linked starches, CAS1, CAS2, CAS3 and CAS4 were synthesized by using ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine, respectively. Adsorptions of acid black 1 (C. I. 20470) onto synthesized acyclic polyamine modified cross-linked starch (CAS) and chitosan were investigated. The optimum initial pH value is 3.0 and the adsorptions reach equilibrium after 3h. The interactions of the amino-polysaccharides with AB1 are electrostatic attraction and the best-fit model is Langmuir isotherm. Chitosan has the highest adsorption capacity of 1078mg•g^{-1} and the capacities of CAS2 and CAS1 are close to chitosan, while CAS4 has the lowest adsorption capacity of 757mg•g^{-1}. The FT-IR spectra demostrate that the amino groups of amino-polysaccharides are protonated and the AB1 molecules were effectively adsorbed.

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References

1. Brown D (1987) Ecotoxicol Environ Saf 13: 139-147
2. Wu TX, Lin T, Zhao JC, Hidaka H, Serpone N (1999) Environ Sci Technol 33: 1379-1387
3. Ramakrishna KR, Viraraghavan T (1997) Water Sci Technol 36: 189-196
4. Vandevivere PC, Bianchi R, Verstraete W (1998) J Chem Technol Biotechnol 72: 289-302
5. Pak D, Chang W (1999) Water Sci Technol 40: 115-121
6. Le Marechal AM, Slokar YM, Taufer T (1997) Dyes Pigm 33: 281-298
7. Zhao X, Qu JH, Liu HJ, Hu C (2007) Environ Sci Technol 41: 6802-6807
8. Asfour HM, Nasser MM, Fadali OA, El-Geundi MS (1985) J Chem Technol Biotechnol 35: 28-35
9. Chu HC, Chen KM (2002) Process Biochem 37: 595-600
10. Guibal E, Saucedo I, Jansson-Charrier M, Delanghe B, Le Cloirec P (1994) Water Sci Technol 30: 183-190
11. Rio S, Faur-Brasquetc C, Le Coq L, Le Cloirec P (2005) Environ Sci Technol 39: 4249-4257
12. Fetterolf ML, Patel HV, Jennings JM (2003) J Chem Eng Data 48: 831-835
13. El Qada EN, Allen SJ, Walker GM (2006) Ind Eng Chem Res 45: 6044-6049
14. Shawabkeh RA, Tutunji MF (2003) Appl Clay Sci 24: 111-120
15. Bae JH, Song DI, Jeon YW (2000) Sep Sci Technol 35: 353-365
16. El Mouzdahir Y, Elmchaouri A, Mahboub R, Gil A, Korili SA (2007) J Chem Eng Data 52: 1621-1625
17. Blackburn RS (2004) Environ Sci Technol 38: 4905-4909
18. Juang RS, Tseng RL, Wu FC, Lee SH (1997) J Chem Technol Biotechnol 70: 391-399
19. Figueiredo SA, Boaventura RA, Loureiro JM (2000) Sep Purif Technol 20: 129-141
20. Wong YC, Szeto YS, Cheung WH, Mckay G (2003) Langmuir 19: 7888-7894
21. Crini G (2005) Prog Polym Sci 30: 38-70
22. Xiang B, Li YJ, Ni YM (2003) Environ Protect Chem Ind 23: 300-303
23. Lertworasirikul A, Tsue S, Noguchi K, Okuyama K, Ogawa K (2003) Carbohydr Res 338: 1229-1233
24. Langmuir I (1918) J Am Chem Soc 40: 1361-1401
25. Giles CH, Smith D, Huitson A (1974) J Colloid Interface Sci 47: 755-765
26. Hinz C (2001) Geoderma 99: 225-243
27. Freundlich HMF (1906) Z Phys Chem 57: 385-470
28. Kumar MNVR (2000) React Funct Polym 46: 1-27
29. Wang S, Li H (2007) Dyes Pigm 72: 308-314
30. Šafaříková M, Ptáčková L, Kibriková I, Šafařík I (2005) Chemosphere 59: 831-835
31. Osaman Z, Arof AK (2003) Electrochim Acta 48: 993-999
32. Vongchan P, Sajomsang W, Subye D, Kongtawelert P (2002) Carbohydr Res 337: 1233-1236